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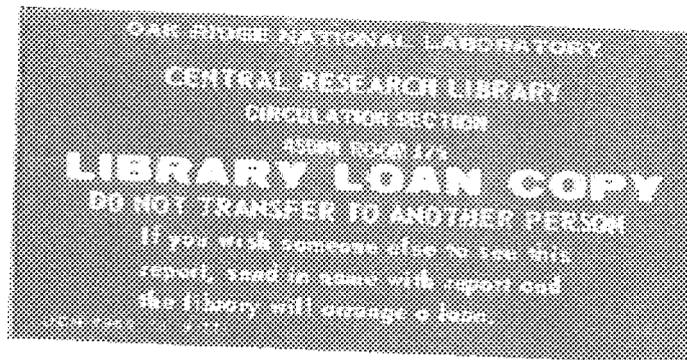
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## Removal of Volatile Organic Compound from Groundwater: A Survey of the Technologies

S. P. Singh  
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REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER: A  
SURVEY OF THE TECHNOLOGIES

S. P. Singh  
R. M. Counce

Date Issued - May 1989

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## NOMENCLATURE

a	gas-liquid interfacial area per unit of packed volume, $\text{m}^2/\text{m}^3$
$a_t$	specific area of packing per unit of packed volume, $\text{m}^2/\text{m}^3$
$a_w$	wetted area of packing per unit of packed volume, $\text{m}^2/\text{m}^3$
C	correction factor for high gas rates
$C_1$	correlation factor in equation for gas-phase mass-transfer coefficient
$d_c$	diameter of column, m
$d_{eq}$	equivalent diameter ( $4r_h$ ), m
$d_p$	diameter of packing, m
$D_L$	liquid-phase diffusivity, $\text{m}^2/\text{s}$
$D_G$	gas-phase diffusivity, $\text{m}^2/\text{s}$
$Fr_L$	Froude number $[(L')^2 a_t/L^2 g]$
$f_1$	$(\mu_L/\mu_w)^{0.16}$ , $\mu_w = 1 \text{ mN/m}^2\text{-s}$
$f_2$	$(\rho_w/\rho_L)^{1.25}$ , $\rho_w = 1000 \text{ kg/m}^3$
$f_3$	$(\sigma_w/\sigma)$ , $\sigma_w = 72.8 \text{ mN/m}$
g	acceleration due to gravity, $9.807 \text{ m/s}^2$
G	superficial gas molar velocity, $\text{kmol/m}^2\text{-s}$
$G'$	superficial gas mass velocity, $\text{kg/m}^2\text{-s}$
H	Henry's constant, $\text{m}^3\text{atm/kmol}$
$H_G$	height of gas-phase transfer unit, m
$H_L$	height of liquid-phase transfer unit, m
$H_{toL}$	height of overall liquid-phase transfer unit, m
$k_G$	individual gas-phase mass-transfer coefficient, $\text{kmol/m}^2\text{-s-atm}$
$k_L$	individual liquid-phase mass-transfer coefficient, m/s
$k_x$	individual liquid-phase mass-transfer coefficient, $\text{kmol/m}^2\text{-s}$ (mole fraction)
$k_y$	individual gas-phase mass-transfer coefficient $\text{kmol/m}^2\text{-s-(mol}$ fraction)
$K_x$	overall liquid-phase mass-transfer coefficient, $\text{kmol/m}^2\text{-s-(mol}$ fraction)
$K_y$	overall gas-phase mass-transfer coefficient, $\text{kmol/m}^2\text{-s-(mol}$ fraction)
L	superficial liquid molar velocity, $\text{kmol/m}^2\text{-s}$
$L'$	superficial liquid mass velocity, $\text{kg/m}^2\text{-s}$



$m$	equilibrium distribution ratio, $y/x$
$M_G$	average gas molecular weight, kg/kmol
$M_L$	average liquid molecular weight, kg/kmol
$N_A$	mass-transfer flux of component A, kmol/m <sup>2</sup> -s
$N_{toL}$	number of overall liquid-phase transfer units, dimensionless
$P_I$	partial pressure of inert, atm
$P_T$	total pressure, atm
$R$	ideal gas-law constant
$Re_G$	gas-phase Reynold's number ( $G'/a_t\mu_G$ )
$r_h$	hydraulic radius, m
$Re'_G$	gas-phase Reynolds number based on the equivalent diameter and gas and liquid velocities through structured packing channels ( $d_{eq}\rho_G/\mu_G$ ) ( $V'_G + V'_L$ )
$Re_L$	liquid-phase Reynolds number ( $L'/a_t\mu_L$ )
$S$	stripping factor - $mG/L$ , dimensionless
$Sc_G$	gas-phase Schmidt number ( $\mu_G/\rho_G D_G$ )
$Sc_L$	liquid-phase Schmidt number ( $\mu_L/\rho_L D_L$ )
$Sh'_G$	Sherwood number based on equivalent diameter ( $k_G d_{eq}/D_G$ )
$T$	temperature, Kelvin, K
$V_G$	superficial velocity of gas, m/s
$V'_G$	effective gas velocity through channel of structured packing, m/s
$V_L$	superficial liquid velocity, m/s
$V'_L$	effective liquid velocity through channel of structured packing, m/s
$We_L$	liquid-phase Weber number, $(L')^2/\rho_L\sigma a_t$
$x$	mol fraction in the liquid phase, kmol/kmol
$y$	mol fraction in the gas phase, kmol/kmol
$z$	length, m
$z_p$	depth of packing per bed, m

#### Greek symbols

$\epsilon$	void fraction, m <sup>3</sup> /m <sup>3</sup>
$\epsilon_L$	liquid holdup, m <sup>3</sup> /m <sup>3</sup>
$\Gamma$	liquid flow rate based on perimeter, kg/m-s
$\mu_G$	gas-phase viscosity, N-s/m <sup>2</sup>



$\mu_L$	liquid-phase viscosity, N-s/m <sup>2</sup>
$\rho_G$	gas density, kg/m <sup>3</sup>
$\rho_L$	liquid density, kg/m <sup>3</sup>
$\rho_w$	1000 kg/m <sup>3</sup>
$\sigma$	surface tension, N/m
$\sigma_c$	critical surface tension of packing material, N/m
$\sigma_w$	0.071 N/m
$\phi$	correlation parameter for a given packing, m
$\psi$	correlation parameter for a given packing, m
$\theta$	angle of structured packing channel with respect to horizontal, degrees

Subscripts

M	logarithmic average
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REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER:  
A SURVEY OF THE TECHNOLOGIES

S. P. Singh and R. M. Counce

ABSTRACT

Groundwater contaminated with volatile organic compounds (VOCs) is being encountered with greater frequency. Since the natural degradation of these contaminants is very slow, artificial means of removing the organic compounds from the groundwater are required to prevent further deterioration of the aquifer. The technologies which have been employed for the removal of VOCs from groundwater are air stripping, biological treatment, carbon adsorption, chemical oxidation, and membrane separation. This report provides a review of the status of these technologies with particular emphasis on air stripping with emissions control.

1. INTRODUCTION

Groundwater has been an important source of freshwater in the past and will continue to be in the future. Groundwater contains close to 95% of the useable freshwater of the world and approximately 50% of the United States population uses it as a source of drinking water (Barbash and Roberts 1986). However, groundwater which is contaminated with industrially produced organic compounds is being encountered with greater and greater frequency. Contamination of groundwater with organic compounds is not limited to vicinities near industrial operations because many of these compounds are present in household consumer products. Some of these compounds show evidence of carcinogenicity, mutagenicity, and teratogenicity and have a very long life span due to low biological and chemical reactivity. The major sources of contaminants are accidental spills, underground storage tanks, waste lagoons, landfills, and septic tanks (Althoff et al. 1981). It used to be that when the water from a particular well was discovered to contain synthetic organic compounds, it was capped and a new well drilled. However, this can no longer be done in many places because a major portion of the groundwater is contaminated. Because groundwater movement is very slow, it may take decades or even centuries for natural processes to eliminate the organic compounds from groundwater. Therefore, when groundwater is the primary source of drinking water for a community, artificial means of removing the organic compounds from water are required. The purpose of this report is to review the technologies available for removing volatile organic compounds

(VOCs) from groundwater with particular emphasis on air stripping with emissions control.

## 2. TREATMENT TECHNOLOGIES

Technologies which have been employed to treat water contaminated with organic compounds include (1) air stripping, (2) biological treatment, (3) carbon adsorption, (4) chemical oxidation, and (5) membrane separation. The type of technology employed in the removal of VOCs from groundwater depends to a large extent on the ultimate use of the treated water. If the water is to be used as a source of drinking water, then almost complete removal (>99%) will be required. Some of the technologies may not be able to meet this requirement when used alone, and thus have to be combined with other technologies to achieve the final product requirement. Also, the choice of technology may be influenced by the generation of secondary pollutants, which may require further treatment or proper disposal. The capital and operating costs of a technology are also a major factor because clean up of groundwater is expected to be a long-term project. Thus these variables, along with site specific requirements, should be used to select the technology which best suits the needs.

### 2.1 AIR STRIPPING WITH EMISSIONS CONTROL

Air stripping is a process by which water contaminated with slightly soluble VOCs may be purified by transferring the contaminant from the water to air. Air stripping was used for aesthetic reasons in the nineteenth century to remove VOCs which imparted taste and odor to the drinking water (McCarty 1983). Since air stripping involves the transfer of the contaminants from the liquid phase to the gaseous phase, intimate contact between the two phases is required. The contact between the two phases may be accomplished by (1) surface aeration, (2) diffused air system, or (3) specially designed liquid-gas contactors. Surface aeration systems are simplest to design, since only an aerator and holding tank are required. The efficiency of the surface aeration system depends upon (1) power-to-volume ratio, (2) type of aerator, (3) temperature, and (4) detention time (Kang et al. 1985). In the diffused air system,

compressed air is bubbled through the holding tank. The efficiency of this system may range from 50 to 85% because of the small interfacial area and the short contact time between the two phases (Gross 1985). The best liquid-gas contact is usually achieved in contactors designed to achieve large interfacial areas. The liquid-gas contactors include (1) bubble columns, (2) spray columns, (3) cooling towers, and (4) packed columns (Fleming 1984). Bubble columns are diffused air systems in which the flow of the two phases may be co-current or counter-current with respect to each other. They are best suited for situations where low removal of the VOCs is required and where high throughputs are desirable (Fleming 1984). In the spray column, the vapor phase is the continuous phase. They are relatively inefficient in the removal of VOCs with the only advantage being low pressure drop for the gas phase through the column. Cooling towers can be an effective method for removal of VOCs from groundwater, and they have been used for removal of 1,1,1-trichloroethane and tetrachloroethylene. The advantages of cooling towers include: (1) low pressure drop for both liquid and gas phases, (2) high turndown potential, (3) wide range of gas to liquid ratios, and (4) high rate of mass flow (Fleming 1984). Packed columns are the most efficient type of liquid-gas contactor. In a packed column, water is broken into a number of slow-moving films which form over the packing, break, and reform. This creates a large amount of interfacial area, which is constantly being renewed. The following section discusses the theory involved in the design of packed columns in more detail and also presents the results of full-scale air stripping columns used for the removal of VOCs.

### 2.1.1 Packed Air Strippers

#### 2.1.1.1 Theory and Design

The design of packed towers is well developed in the chemical engineering literature (Treybal 1980, Chohey and Hicks 1984, Fair et al. 1984). A typical packed tower is shown in Fig. 1. The design process for strippers usually begins with known liquid flow rate and composition information including that of the solute to be removed. The first step consists of the selection of the stripping medium; in this section, it is generally assumed that air is that medium. The air flow rate is selected such that an adequate "driving force" for this operation can be

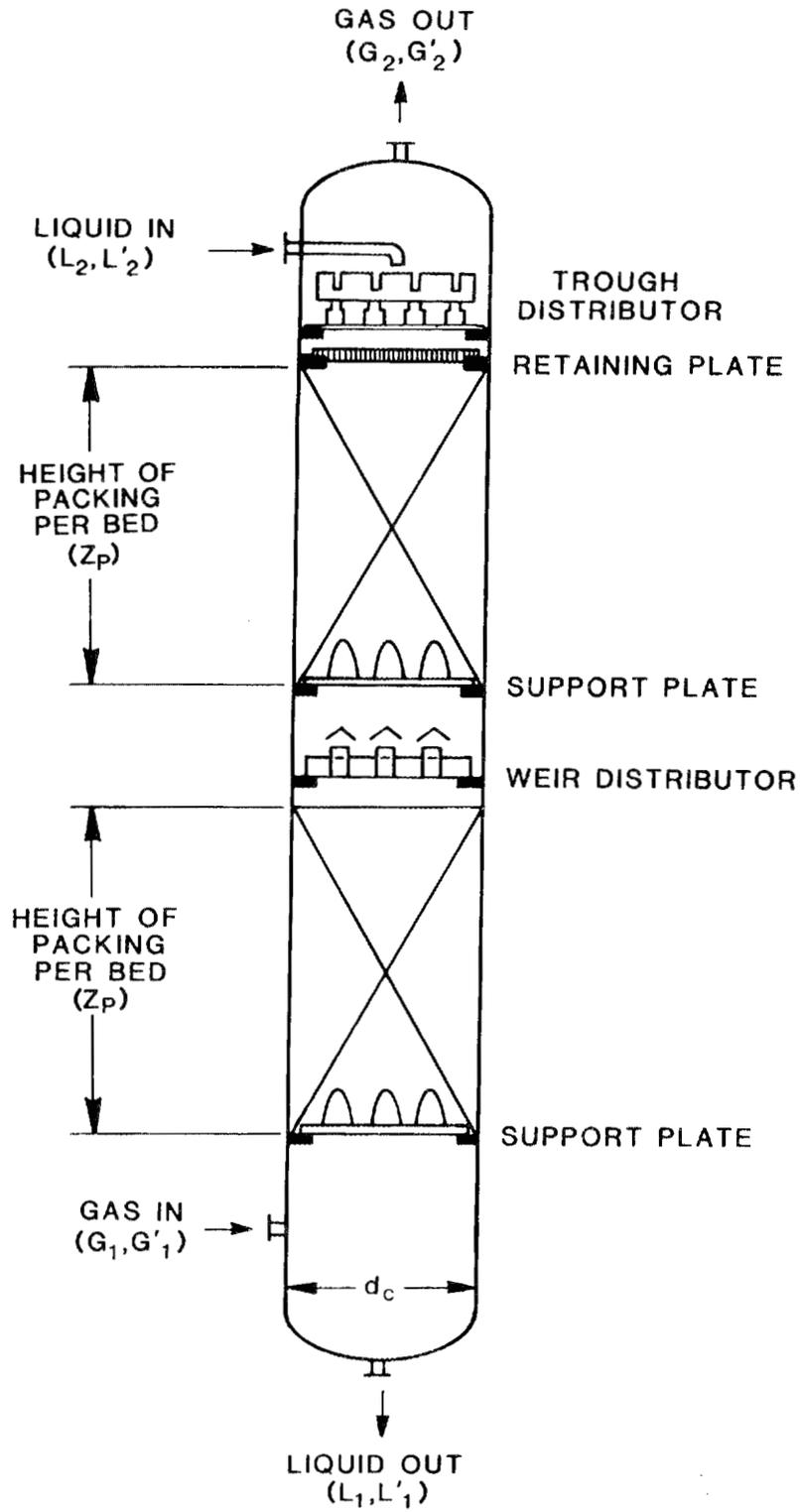


Fig. 1. Typical packed towers.

maintained. For conditions as typically existing in air strippers, this may be satisfied by choosing a stripping factor  $>1$ . The stripping factor is defined by

$$S = mG/L \quad (1)$$

The stripping factor contains a ratio of the gas and liquid superficial molar velocities; it is helpful to note that this ratio is identical to that of the molar flow rates of these two phases, since the tower cross-sectional area is not often known in the early stages of the design process. The optimum value of  $S$  is frequently found to be between 1.25 and 2 (Colburn 1939).

Two general types of packing are useful for VOC removal by air stripping - random and structured packings. Random packings come in a number of varieties, with standard saddles and slotted rings most commonly used for commercial applications; the commercial names may vary with the manufacturer, such as Flexirings<sup>®</sup> from Koch Engineering Company vs Pall rings from Chemical Processing Products Division of Norton Company, and Flexisaddles<sup>®</sup> from Koch Engineering Company vs Intalox<sup>®</sup> saddles from Norton Chemical Process Products or Novalox<sup>®</sup> saddles from Jaeger Products, Inc. Random packing is sometimes referred to as "dumped" packing due to the usual method of placement in the tower. Random packings are available in a number of nominal sizes or diameters,  $d_p$ , up to 89 mm and in materials of ceramic, plastic, or metal. When placed in the tower, the number of pieces of random packing per unit volume is less in the immediate vicinity of the tower wall; this condition leads to a tendency of the liquid to segregate toward the walls of the tower (Treybal 1980). This tendency is less when the ratio of  $d_c/d_p$  is  $>8$  according to Treybal (1980), with the "best" value occurring at 15; Eckert (1961) recommends minimum  $d_c/d_p$  values of 30 for Raschig rings, 15 for standard saddles (other than Raschig rings) and 10 to 15 for slotted rings. In view of the tendency of the liquid and gas flows to segregate in packed towers, it is customary to redistribute the liquid at intervals,  $Z_p$ , varying from 2.5 to 10 times the tower diameter; Eckert (1961) recommends maximum  $Z_p/d_c$  values of 2.5 to 3 for Raschig rings, 5 to 8 for standard saddles (other than Raschig rings), 5 to 10 for slotted rings, or 6 m, whichever is smaller.

There is still speculation over the extent that good initial liquid distribution can affect the maximum  $Z_p/d_c$  ratio (Strigle 1987).

Structured packings offer advantages of low pressure-drop service, and usually have excellent liquid distribution characteristics. These packings are manufactured as elements which are carefully fitted to the inside dimensions of the tower in an ordered or structured manner. An example of such a packing fabricated from corrugated sheets is shown in Figure 2. These sheets are commonly made of metal gauze (woven wire cloth) or sheet metal as well as various plastics. The gauze packings are sometimes referred to as "high efficiency" packing; an example of such material is the Koch-Sulzer packing. The cloth nature of the surface promotes a capillary action so that the liquid covers the available surface even at low liquid loading; the type of liquid flow inherent in such material appears to greatly enhance liquid-phase transport (Bravo et al. 1985; Selby and Counce 1986). Similar packing elements fabricated of sheet metal or plastic do not appear to have the reduced liquid-phase resistance and near constant interfacial area properties of the gauze-type packings. The gauze-type structured packing is more expensive than either sheet-metal or plastic-structured packing or dumped packing; its use, however, can significantly reduce design height requirements.

Discussion of typical tower intervals, distributors, packing support etc., is presented by Treybal (1980) and Perry et al. (1984). The design of these items is critical for efficient packed tower operation (Kunesh et al. 1987, Kunesh 1987). They are usually manufactured and distributed by the same commercial concerns that supply tower packing. The flow-through type of packings such as Pall® rings, metal Intalox® saddles, and structured packings require that more attention be paid to the distribution of both gases and liquids than for older types of packings (bluff-body packings) such as Raschig rings, Berl saddles, and ceramic Intalox saddles. These older types of packings forced fluids to flow around them, causing a higher pressure loss and provided more capacity to correct for maldistribution (Fair 1989). Entrainment eliminators are not essential for VOC removal in the stripper, but they may be very important for equipment operating downstream from the stripper tower. Knitted wire mesh is especially effective for removing entrained droplets of liquid from gas streams, although many other devices are available; further

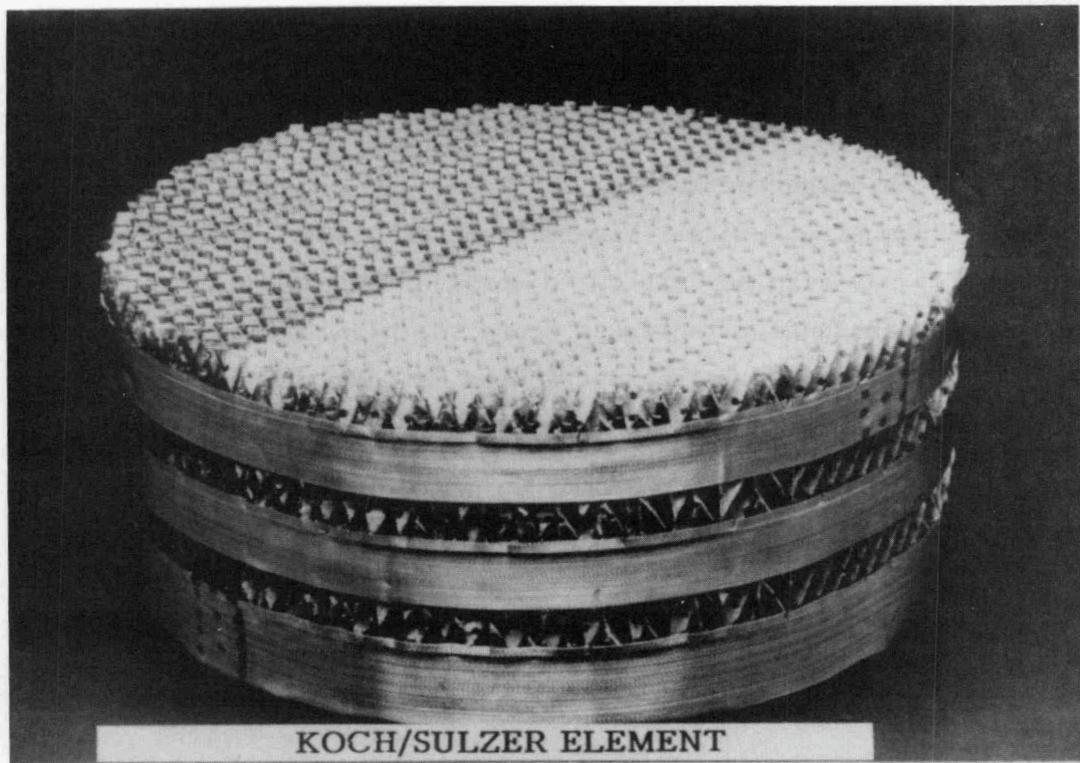
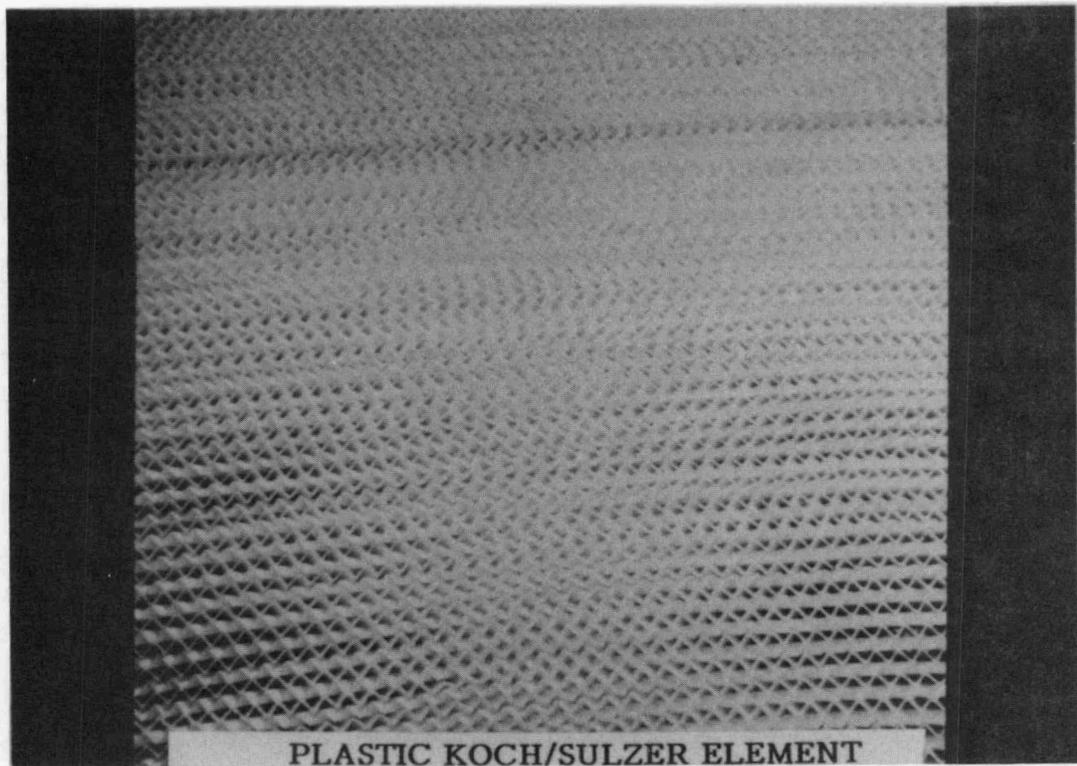


Fig. 2. Examples of structured packing.

discussion on this subject is found in Treybal (1980) and Fair et al. (1984).

Packed towers are usually circular in cross-section due to ease of construction and strength (Treybal 1980). The diameter of a tower for fixed gas and liquid rates is normally bounded by limits of operability. At a sufficiently small diameter, the tower will flood. At too large a diameter, the packing will not be sufficiently wetted for efficient mass transfer. Towers have operated with superficial liquid velocities as low as 0.18 mm/s; however, special liquid distribution systems are required (Norton Company 1971). Usually, the tower is designed to operate at a given differential pressure drop per meter of packing; typical values for strippers of 200 to 400 Pa per meter of packed depth are common (Treybal 1980). Alternately, the tower may be designed by selecting a gas velocity as a fraction of the flooding gas velocities; design values of 50 to 80% are common.

The height of packing required for a given separation may be conveniently calculated using the transfer unit concept (see also Appendix A),

$$Z = H_{toL} N_{toL}, \quad (2)$$

where  $Z$  is the height of packing required, and  $H_{toL}$  and  $N_{toL}$  are the height and number of overall liquid transfer units. The above relationship may also be written in terms of overall gas transfer units; the form chosen usually indicates where the principal resistance lies. The height of an overall liquid transfer unit may be calculated from estimates of heights of individual gas and liquid transfer units,

$$H_{toL} = H_L + H_G/S . \quad (3)$$

Alternately  $H_{toL}$  may be estimated by an overall coefficient approach,

$$H_{toL} = L/K_x a . \quad (4)$$

The overall coefficient is related to individual coefficients, interfacial area, and the equilibrium distribution ratio by

$$\frac{1}{K_{xa}} = \frac{1}{k_{xa}} + \frac{1}{mk_{ya}} \quad (5)$$

The equilibrium distribution ratio,  $m$ , is related to Henry's constant,  $H$ , by

$$m = y/x = H(\rho_L/M_L P_T) \quad (6)$$

The Henry's law constant determines the distribution of the solute between the gas and liquid phases and depends upon the nature of the solute and the temperature. Although the Henry's law constant can be estimated from the vapor pressure of pure solute and the solubility of the solute in water, experimental determination is usually recommended. Experimentally determined expressions for the variation of Henry's law constants with temperature for compounds which may be encountered in groundwater cleanup are given in Tables 1 to 3.

Further information on estimates of  $H_L$ ,  $H_G$ ,  $k_x$ ,  $k_y$  and  $a$  can be found in Appendix B.

The number of transfer units at conditions common to VOC removal is

$$N_{toL} = \int_{x_1}^{x_2} \frac{dx}{x - y/m} \quad (7)$$

This concept is treated further in Appendix A. In its simplest form, the number of transfer units is the change in liquid phase solute composition divided by the average solute driving force composition.

The design of packed towers usually includes a substantial safety factor to account for uncertainties in the data base. Bolles and Fair (1982) state that the calculated height should be multiplied by 1.7 or 2.2 to achieve 95% confidence when using their correlations for  $H_L$  and  $H_G$  or the models of Onda et al. (1968), respectively. Harriott (1987) studied several sets of VOC stripping data and concluded that the liquid maldistribution is inherent in packed towers and its effect is significant at stripping factors less than 3. He presents a safety factor of  $(1 + 0.9/S)$ .

Table 1. Coefficients<sup>a</sup> for the temperature dependence of Henry's Law Constant expression for the temperature range from 0 to 30°C (1 atm)

Compound	A	B
1,1,1-trichloroethane (1,1,1-C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> )	21.68	4375
1,1-dichloroethylene (1,1-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )	23.12	4618
trichloroethylene (C <sub>2</sub> HCl <sub>3</sub> )	21.89	4647
tetrachloroethylene (C <sub>2</sub> Cl <sub>4</sub> )	22.68	4735
methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	17.42	3645
chloroform (CHCl <sub>3</sub> )	18.97	4046
carbon tetrachloride (CCl <sub>4</sub> )	22.22	4438
ethylene dichloride (1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	16.05	3539
1,1,2-trichloroethane (1,1,2-C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> )	16.20	3690
<u>s</u> -tetrachloroethane ( <i>s</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub> )	14.91	3547
1,2-dichloropropane (1,2-C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> )	19.60	4333
1,3-dichloropropane (1,3-C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> )	17.13	3917
1,2,3-trichloropropane (1,2,3-C <sub>3</sub> H <sub>5</sub> Cl <sub>3</sub> )	14.61	3477
1-chlorobutane (1-C <sub>4</sub> H <sub>9</sub> Cl)	18.51	3482
2-chlorobutane (2-C <sub>4</sub> H <sub>9</sub> Cl)	22.29	4499
1,4-dichlorobutane (1,4-C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> )	13.79	3128
1-chloropentane (1-C <sub>5</sub> H <sub>11</sub> Cl)	23.04	4727
1,5-dichloropentane (1,5-C <sub>5</sub> H <sub>10</sub> Cl <sub>2</sub> )	8.79	1597
1-chlorohexane (1-C <sub>6</sub> H <sub>13</sub> Cl)	22.16	4459
benzene (C <sub>6</sub> H <sub>6</sub> )	19.02	3964
chlorobenzene (C <sub>6</sub> H <sub>5</sub> Cl)	16.83	3466
toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	18.46	3751
<i>o</i> -chlorotoluene ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )Cl)	17.18	3545

<sup>a</sup> $a_m = y/x = \exp [A - B/T]$  where T is in K.

Source: Leighton, D. T. and J. H. Calo, "Distribution Coefficients of Chlorinated Hydrocarbons in Dilute Air-Water Systems for Ground-water Contamination Application," J. Chem. Eng. Data, 26(4), 382-5, 1981.

Table 2. Henry's Law Constant as a function of temperature  
for the temperature range from 10 to 35°C

Compound	Temperature dependence <sup>a</sup> regression equation (T, K) $H = \exp(A - B/T)$	
	A	B
tetrachloroethylene	12.45	4918
trichloroethylene	11.37	4780
1,1-dichloroethylene	8.845	3729
cis-1,2-dichloroethylene	8.479	4192
trans-1,2-dichloroethylene	9.341	4182
vinyl chloride	7.385	3286
1,1,1-trichloroethane	9.777	4133
1,1-dichloroethane	8.637	4128
chloroethane	5.974	3120
carbon tetrachloride	11.29	4411
chloroform	9.843	4612
dichloromethane	6.653	3817
chloromethane	9.358	4215

<sup>a</sup>The units for the Henry's Law Constant are m<sup>3</sup>-atm/mol.

Source: Gossett, J. M., "Measurement of Henry's Law Constants for C<sub>1</sub> and C<sub>2</sub> Chlorinated Hydrocarbons," Environ. Sci. Technol. 21(2), 202-208, 1987.

Table 3. Component parameters for the temperature regression equation  
Temperature regression parameters<sup>a</sup>

Component	A	B	r <sup>2</sup>
nonane	- 0.1847	202.1	0.013
n-hexane	25.25	7530	0.917
2-methylpentane	2.959	957.2	0.497
cyclohexane	9.141	3238	0.982
chlorobenzene	3.469	2689	0.965
1,2-dichlorobenzene	-1.518	1422	0.464
1,3-dichlorobenzene	2.882	2564	0.850
1,4-dichlorobenzene	3.373	2720	0.941
o-xylene	5.541	3220	0.966
p-xylene	6.931	3520	0.989
m-xylene	6.280	3337	0.998
propylbenzene	7.835	3681	0.997
ethylbenzene	11.92	4994	0.999
toluene	5.133	3024	0.982
benzene	5.534	3194	0.968
methyl ethylbenzene	5.557	3179	0.968
1,1-dichloroethane	5.484	3137	0.993
1,2-dichloroethane	-1.371	1522	0.878
1,1,1-trichloroethane	7.351	3399	0.998
1,1,2-trichloroethane	9.320	4843	0.968
cis-1,2-dichloroethylene	5.164	3143	0.974
trans-1,2-dichloroethylene	5.333	2964	0.985
tetrachloroethylene	10.65	4368	0.987
trichloroethylene	7.845	3702	0.998
tetralin	11.83	5392	0.996
decalin	11.85	4125	0.919
vinyl chloride	6.138	2931	0.970
chloroethane	4.265	2580	0.984
hexachloroethane	3.744	2550	0.768
carbon tetrachloride	9.739	3951	0.997
1,3,5-trimethylbenzene	7.241	3628	0.962
ethylene dibromide	5.703	3876	0.928
1,1-dichloroethylene	6.123	2907	0.974
methylene chloride	8.483	4268	0.988
chloroform	11.41	5030	0.997
1,1,2,2-tetrachloroethane	1.726	2810	0.194
1,2-dichloropropane	9.843	4708	0.820
dibromochloromethane	14.62	6373	0.914
1,2,4-trichlorobenzene	7.361	4028	0.819
2,4-dimethylphenol	-16.34	-3307	0.555
1,1,2-trichlorotrifluoroethane	9.649	3243	0.932

Table 3 (continued)

Component	A	B	r <sup>2</sup>
methyl ethyl ketone	-26.32	-5214	0.797
methyl isobutyl ketone	-7.157	160.6	0.002
methyl cellosolve	-6.050	-873.8	0.023
trichlorofluoromethane	9.480	3513	0.998

<sup>a</sup>Temp. regression equation:  $H = \exp(A - B/T)$ , H in atm-m<sup>3</sup>/mol, T in K.

Source: Ashworth, R. A., G. B. Howe, M. E. Mullins, and T. N. Rogers, "Air-Water Partitioning Coefficients of Organics in Dilute Aqueous Solutions," to be published in J. of Haz. Mater.

The data base for estimation of mass transfer information is often not available for new packing. Advertisement for new packing often gives overall coefficient information; this data, however, usually involves the absorption of CO<sub>2</sub> into caustic solutions where liquid-phase resistance to mass transfer is minimal and, thus, is inappropriate for general use in the design of air strippers for VOC removal.

In general, inexpensive saddles and slotted rings which have long been reliably used in industry, appear to be cost effective for VOC strippers (Hill 1987). Speciality random packings, however, are continually being developed and marketed; these packings are usually much higher priced than "standard" types of packing. The economics of the use of speciality random packings should be carefully investigated before they are specified and used. The major use of structured packings for VOC stripping appears to be to repack existing towers where greater efficiency or more capacity is required (Hill 1987). Another use of structured packings may be for situations where minimum space exists for the stripper.

#### 2.1.1.2 Packed Columns

Full- and pilot-scale packed columns have been designed and operated at sites in both the United States and Europe. A recent survey for the Environmental Protection Agency identified 177 air stripper systems in the United States (EPA-450/3-87-017). The report did not indicate what fraction of the total air stripper systems were still operating. This section describes a few full-scale air stripper systems on which information is available in the literature.

Netherlands, Europe: A full-scale column was placed in operation in April 1983, to remove tetrachloroethylene (170 ppb) and trichloroethylene (95 ppb) from groundwater. The concentration of tetrachloroethylene and trichloroethylene was reduced to 0.5 ppb and 0.3 ppb, respectively. The column design parameters were:

Diameter of the tower	1.6 m
Packing	30 mm Hy-Pak
Height of packing	3.7 m

Total height of tower	6.4 m
Water loading	36 m <sup>3</sup> /h
Air loading	3000 m <sup>3</sup> /h
Air/water ratio	80 (vol/vol)

The estimated capital and maintenance costs were Dfl. (Dutch Florin) 0.05 per cubic meter of water, and the energy usage was 0.2 kJ per cubic meter of water (Reijnen et al. 1985).

Tacoma, Washington: Five air stripping towers for the removal of 1,1,2,2 tetrachloroethane (17-300 ppb), 1,2-trans-dichloroethylene (30-100 ppb), trichloroethylene (54-130 ppb), and tetrachloroethylene (1.6-5.4 ppb) went into operation in 1983. The column design criteria were:

Column diameter	3.7 m
Packing	25.4 mm polypropylene saddles
Packing depth	6.4 m
Water loading	159 m <sup>3</sup> /h
Air loading	49,000 m <sup>3</sup> /h (at STP)
Air/water ratio	310 (vol/vol)

Over 94 percent of 1,1,2,2-tetrachloroethane was removed and the concentrations of the other contaminants in the effluent from the column were below the detection limits. The total capital cost of the facility, including associated construction management services was \$929,000 (1987 dollars) (Rosain and Morton, 1984).

Rockaway Township, New Jersey: An air stripper for removal of methyl-tertiary-butyl ether (up to 40 ppb), diisopropyl ether (up to 70 ppb), and trichloroethylene (200-300 ppb) went into operation February 1984. The tower design parameters were

Tower diameter	2.7 m
Packing	76.2 mm polyethylene Tellerettes
Packing depth	7.6 m
Water loading	320 m <sup>3</sup> /h
Air loading	63,680 m <sup>3</sup> /h
Air/water ratio	200 (vol/vol)

The capital cost for the equipment was estimated in 1981 to be \$404,000 (1987 dollars) and the power consumption, based on \$0.03/MJ, was \$100,000 annually (McKinnon and Dyksen, 1984).

Wurthsmith Air Force Base, Oscoda, Michigan: In 1982, a full-scale air stripper was installed for removal of trichloroethylene (up to 6000 ppb). Two towers which could be operated in series or parallel were installed. The column design parameters were:

Tower diameter	1.5 m
Packing depth	5.5 m
Packing type	16 and 25 mm Pall rings
Water loading (series)	67-136 m <sup>3</sup> /h
Air loading	479-3470 m <sup>3</sup> /h
Air/water ratio	10-25 (vol/vol)

With the towers operating in series, 99.97% removal of trichloroethylene was achieved. The estimated capital cost of the equipment was \$202,000 (1987 dollars) and the operating cost, based on \$0.014/MJ, was \$30,000 (Gross and TerMaath, 1985).

Biological growth, which caused additional pressure drop, was discovered during operation with the 16 mm packing. After cleaning the packing, constant chlorination of the influent water was required to prevent reoccurrence of the growth. Solids deposition due to iron precipitation was encountered with the operation of the full-size towers and a smaller column at a different location on Wurthsmith Air Force Base (Stallings and Rogers 1985). These findings may indicate that a pretreatment step to remove iron and manganese may be required for long-term operation of packed tower air strippers.

#### 2.1.1.3 Rotary Air Stripper

In a packed column, the flow of the liquid phase through the column is due to gravity. Since the gravitational field of the earth is constant, the surface area of the packing and the gas velocity which can be used in column operation without flooding are limited. The rotary

liquid-gas contactor uses centrifugal force instead of gravity to drive the liquid through the packing. The high centrifugal force causes the formation of very thin liquid film which results in rapid and frequent renewal of the wetted surfaces. The motion of the rotor also causes a high degree of turbulence in the gas phase which decreases the depth of the packing required to achieve a given removal. A rotary liquid-gas contactor was invented by Imperial Chemical Industries in response to a request by the American space program for equipment which could be used in zero gravity environment. This contactor is being marketed by Glitsch Inc. of Dallas, Texas under the generic name HIGEE (high 'g'). A schematic of the HIGEE is shown in Figure 3. The liquid phase is fed into the center of the rotating packing and flows outward while the gas flow is introduced in the housing and flows inward through the packing. The inner radius and the axial length of the packing determine the cross sectional area available for flow and thus the hydraulic capacity of the unit. The packing material of the HIGEE unit must be able to withstand the high gravitational forces which are encountered during operation. The packing material of the HIGEE unit is made of thin layers of porous metal which is wound around to give the proper packing thickness. The metal layers are typically 2 to 10 mm thick and have a specific surface area between 1640 to 3940  $\text{m}^2/\text{m}^3$  (Bucklin and Johnston 1987). The advantages of the HIGEE unit include (1) high capacity for a very small device; (2) low weight; (3) wide turndown ratio; and (4) modular design, making expansion easy and less expensive. The disadvantages of the HIGEE unit are (1) possible mechanical failures and (2) additional power required for the drive motor.

The HIGEE unit has been used in the chemical industry to remove hydrogen sulfide from natural gas and carbon dioxide from sour gases by use of a suitable amine (Bucklin and Johnston 1987). There has been only one test where the HIGEE unit was used for air stripping of volatile organics from groundwater. This test was conducted at a United States coast guard air station in East Bay Township, Michigan, to remove benzene, toluene, xylenes, trichloroethylene, 1,2-dichloroethane, and tetrachloroethylene from groundwater (Dietrich et al. 1987). The design criteria for the stripper were:

ORNL DWG 88-1080

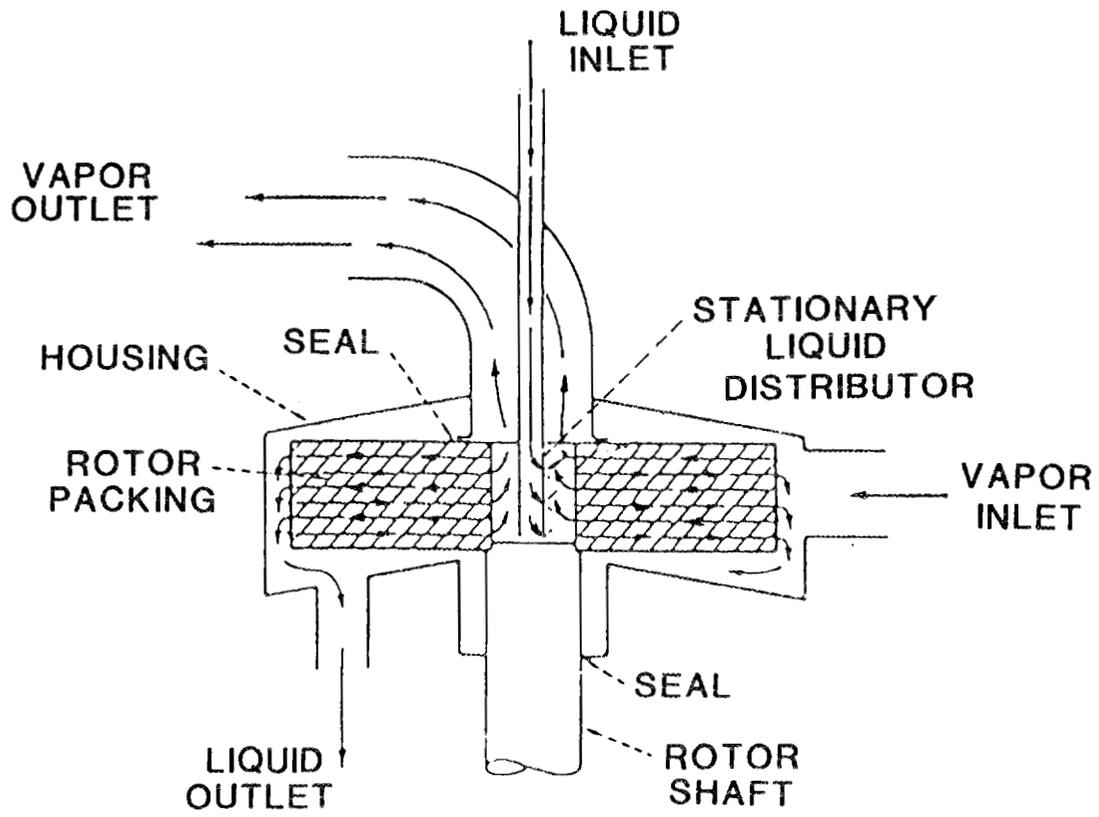


Fig. 3. Rotary air stripper.

Liquid flow rate	22.7 m <sup>3</sup> /h
Gas flow rate	3398 m <sup>3</sup> /h (at STP)
Percent toluene removal	99.5%

To achieve these throughputs and removal, a stripper with the following characteristics was used:

Outside packing diameter	0.8 m
Inside packing diameter	0.28 m
Axial length	0.32 m
Voidage of packing	0.9 to 0.95
Specific surface area	2500 m <sup>2</sup> /m <sup>3</sup>

Removal efficiency of greater than 99% was achieved for all the contaminants, except for 1,2-dichloroethylene, at a gas to liquid ratio of 30:1 and rotor speed of 435 rpm. At constant air to water ratios, an increase in the rotational speed of the rotor above 700 rpm was found to increase the removal efficiency only slightly. Increasing the air to water ratio above 40:1 (vol/vol), produced little effect on the removal efficiency at constant rotor speed. The overall mass transfer coefficient based on the liquid side was calculated using the inlet and outlet concentrations, and was found to vary with the rotor speed at constant gas to liquid ratio, and with gas to liquid ratio at constant rotor speed.

Although no great problems were encountered in the operation of the rotary air stripper, the carryover of the water in the air effluent stream was significant. This may be a problem when emission control devices are used in conjunction with the rotary air stripper.

There is not enough data available on the cost of the rotary air stripper to make a good comparison with packed columns.

#### 2.1.2 Emission Controls

Although air stripping is an effective technology for removing VOCs from groundwater, it simply transfers the contaminant from water to air. Because the quantity of air used in air stripping is large, the concentration of the VOCs in air is usually low. However, if the air stripping towers are located near a large population area, then removal of

the VOCs from the air may be necessary to reduce the exposure to these chemicals. Emission control technologies have been used by industries which use solvents or other VOCs in production processes to either recover or destroy these compounds. The three most commonly used techniques for controlling VOCs from air streams are (1) adsorption onto activated carbon, (2) catalytic destruction, and (3) thermal destruction. This section reviews these technologies and their application to emission control from air stripping processes.

#### 2.1.2.1 Activated Carbon

Activated carbon can be produced from petroleum fractions, wood, coconut shell, and coal and then given treatment by superheated steam, which extends the pore network of the particles and gives activated carbon a large surface area.

The use of activated carbon to remove solvents from air streams is well established and has been in use since the 1930s (Metcalf and Wilkins 1984). The adsorption of the solvent molecules onto the activated carbon is mainly due to Van der Waal forces and no chemical reaction takes place. The adsorption of the VOCs from the gas stream on the activated carbon bed depends upon (1) the type of carbon, (2) relative humidity, (3) temperature, (4) concentration and type of volatile organic compound, and (5) the regeneration steps used (Foster 1985).

Several equations are available in the literature to describe the adsorption of compounds on the activated carbon. These include the Braunauer-Emmett-Teller (BET) equation, Freundlich equation, Langmuir equation and Dubinin-Radushkevich equation (Werner). The isotherm that best describes the adsorption of VOCs from gas streams is the Dubinin-Radushkevich isotherm (Foster 1985). The Dubinin-Radushkevich isotherm can be written as

$$W = W_0 \exp [B e^2/\beta] , \quad (8)$$

where  $W$  = adsorption space occupied by the adsorbate,  $m^3/kg$ ,

$W_0$  = maximum space available,  $m^3/kg$ ,

$B$  = microporosity constant,  $mol^2/cal^2$ ,

$\beta$  = affinity coefficient (ratio of energy of the interaction of the adsorbate molecule with the adsorbent surface to energy interaction of a reference molecule with the same adsorbent surface.

$e$  = adsorption potential =  $RT \ln(P_S/P)$ ,

$R$  = gas constant, cal/mol K,

$T$  = temperature, K,

$P_S$  = saturation vapor pressure of solute at temperature  $T$ , mm Hg,

$P$  = partial pressure of solute in gas, mm Hg.

The maximum space available for adsorption ( $W_0$ ) and the microporosity constant are a function of the nature of the adsorbent. The affinity coefficient can be determined from the polarizability of the adsorbate and a reference compound using the following equation:

$$\beta = \mu/\mu^*, \quad (9)$$

where

$\mu$  = polarizability of the adsorbate,

$\mu^*$  = polarizability of the reference molecule.

The polarizability of any compound can be calculated from the refractive index using the following equation:

$$\mu = [(n^2 - 1) * M] / [(n^2 + 2)\rho_L], \quad (10)$$

where

$n$  = refractive index,

$M$  = molecular weight,

$\rho_L$  = liquid density of the compound.

The adsorption of VOCs from the vapor phase can be affected by the relative humidity. This effect can be explained by noting the adsorption mechanism of water from the gas stream. At low relative humidity, the removal of water from the vapor phase is due mainly to adsorption on the surface of the adsorbent. Due to a relatively low number of hydrophilic sites available on the activated carbon surface, the adsorption of water

is fairly low. As the concentration of the water in the vapor phase increases, capillary condensation begins to occur in the pores of the activated carbon; and the sites available for direct adsorption of the organic molecules from the vapor phase are reduced. The capillary condensation of water increases the resistance to mass transfer of other components in the pores because the compound must first dissolve in the water and then travel through the water to the adsorption site. The reduction in the adsorption of VOCs from the vapor phase decreases rapidly as the relative humidity rises above 50% (Cortright et al. 1985). Thus, the lifetime of the adsorption bed can be extended by lowering the relative humidity of the gas stream, which can be accomplished by raising the temperature of the gas stream. Increasing the temperature too much, however, can also reduce the adsorption capacity. The temperature and relative humidity need to be adjusted to obtain the optimum adsorption capacity.

The various VOCs in the vapor phase also compete with each other for the adsorption sites available. Battelle Columbus Laboratories (1987) studied the adsorption of benzene, ethylbenzene, toluene, trichloroethylene, and 1,1-dichloroethylene from a vapor phase mixture on ten activated carbons. The results of this study indicated that specialty carbons provided no special advantage over the standard carbons. The results also indicated that the breakthrough times for the more volatile components were considerably reduced when other organic compounds were present. The study also noted that the concentration of the more volatile components in the effluent stream from the activated carbons can be significantly higher than the inlet stream once other components start to replace them on the adsorption sites. This observation indicates that experimental determination of the adsorption capacity bed will usually be required when more than one volatile organic compound is present.

Once the adsorption capacity of the activated carbon bed has been determined, a decision has to be made on whether to throw away the carbon or regenerate it when it becomes saturated.

#### Non-regenerative

In most cases the amount of activated carbon used for vapor phase removal is small enough so that throwing away the spent carbon is a viable

economic option. However, other variables such as disposal of the spent carbon, which may be a hazardous waste, needs to be considered. One option available may be the regeneration of the carbon by the vendor. This option may be less expensive than on-site regeneration.

#### Regenerative

If large quantities of activated carbon will be required, then on site regeneration may be the most viable option. Several methods of regenerating the carbon are available including: (1) steam-regeneration, (2) inert gas regeneration, and (3) supercritical fluid regeneration.

Steam-Regeneration. The regeneration of activated carbon using steam is fairly common and is a well-developed process. In this scheme, the bed is regenerated by heating the carbon to about 220°F (104°C) with steam. The flow of the steam is usually in the reverse direction as the loading air stream. At the end of the steam application cycle, the bed is dried and cooled. The cooling and drying periods may be important in the overall operating efficiency of the bed because the adsorption capacity of the carbon may be reduced without these steps (Foster 1985). The disposal of liquid waste generated during the regeneration step and the initial capital investment are the major disadvantages of steam regeneration. Also, the operation and maintenance of this system requires fairly well-trained operators.

Inert Gas - N<sub>2</sub>. The Rekusorb Process, which was invented in Germany, uses nitrogen gas to reactivate the carbon and recover the solvent. A schematic diagram of the process is shown in Figure 4. Howard (1984) describes the desorption of the solvent from the bed as follows:

"The first adsorber (loaded) is now ready to be desorbed and this is achieved by passing nitrogen rich gas through the adsorber and through the activated carbon, purging the vessel. ...The nitrogen rich gas is circulated through the system being progressively heated. The water is less firmly adsorbed and is therefore, preferentially removed prior to desorption of the solvent. The water is then re-adsorbed in the molecular sieve.

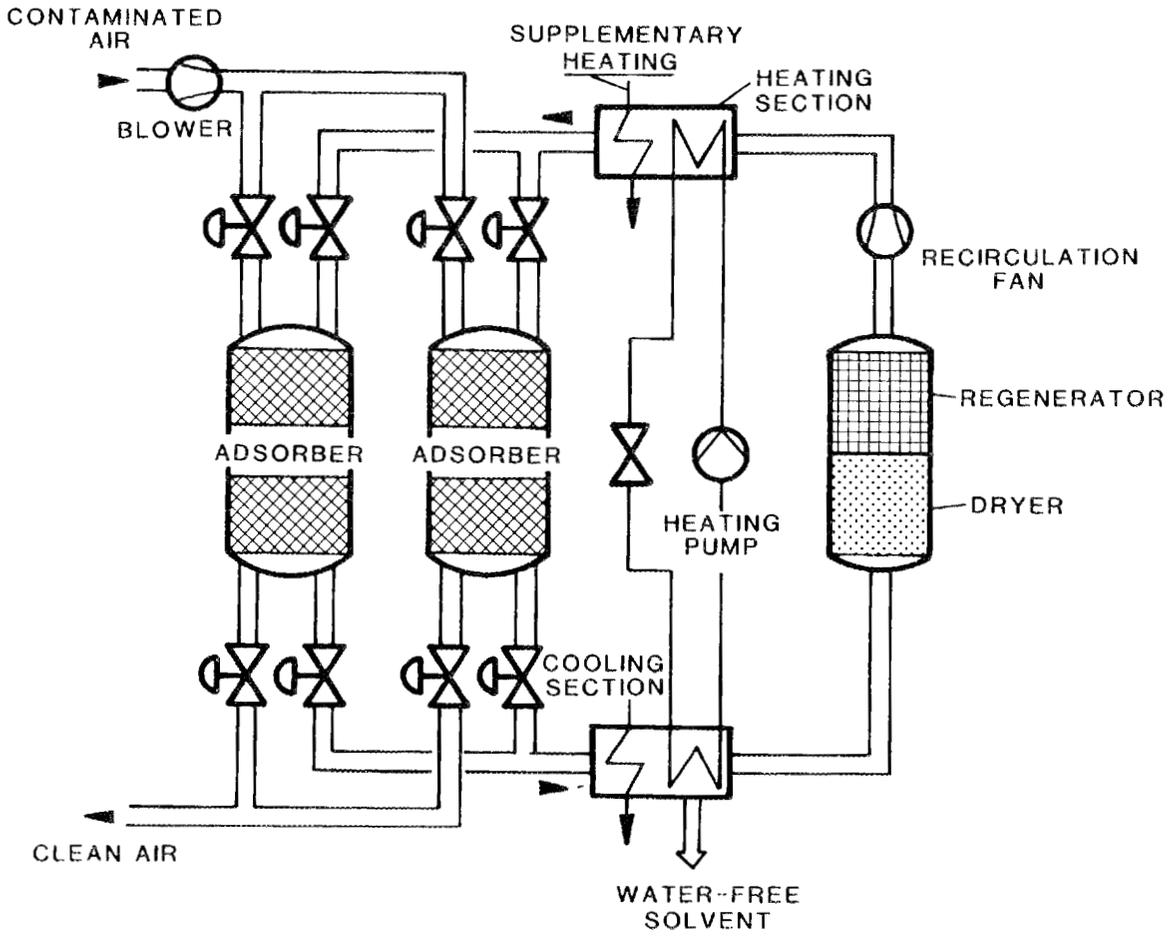


Fig. 4. The Rekusorb Process.

As the nitrogen temperature is increased by the heat pump, plus supplementary heating, the solvent is desorbed and carried to the condenser where it is cooled by the heat pump plus cooling water and removed for reuse... Circulation of the nitrogen rich gas is continued, extracting the heat from the desorbed carbon through the dryer and regenerator. Water is driven out of the dryer and used to prehumidify the adsorber whilst the regenerator stores the heat for the next cycle. The whole process is automatic and continuous."

The advantages of the Rekusorb process include recovery of the solvent in pure form, no secondary pollution is created, energy usage is less than other processes and the risk of explosions is removed. This process may be more competitive when the concentration of the volatile organics is fairly high.

Supercritical Fluids. A supercritical fluid is a substance which has been heated above its critical temperature and compressed beyond its critical pressure. At these conditions, there exists only a single phase as shown in Figure 5. This single phase possesses some properties which are characteristic of liquids (high solubilities of solutes) and some properties which are characteristic of gases (high molecular diffusivity and low viscosity). In the supercritical region, density of the fluid is a strong function of pressure. The very large changes in density with pressure results in correspondingly high changes in solute solubility. This property makes supercritical fluids excellent solvents for extracting and purifying solutes. In addition, the high molecular diffusivity of the supercritical fluid results in mass transfer coefficients which are one to two orders of magnitude higher than those of regular liquids because of its low viscosity.

Although any substance could theoretically be used for a supercritical fluid extraction process, the operating conditions often limit the choices. The supercritical fluid that may find a wide use in regeneration of spent carbon beds is carbon dioxide, whose supercritical temperature and pressure are 30°C and 72.8 atm. This means that supercritical fluid regeneration using carbon dioxide can be accomplished

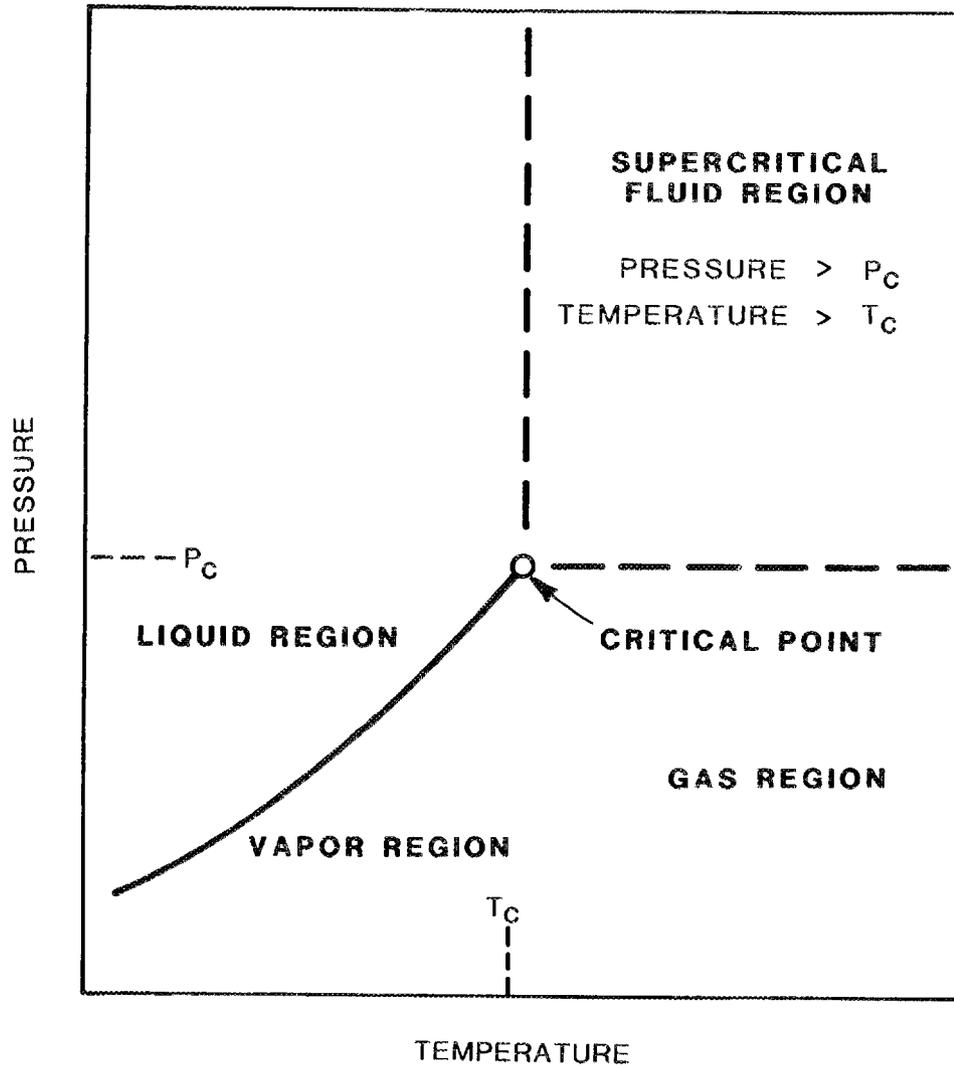


Fig. 5. Vapor pressure curve.

without large inputs of energy. The results of the cyclic adsorption/regeneration of phenol on activated carbon is shown in Fig. 6. It can be seen from Fig. 6 that some of the phenol is irreversibly adsorbed on the activated carbon and is not removed by the supercritical carbon dioxide. However, after the first regeneration, there is no appreciable loss of the adsorption capacity of the activated carbon. Researchers at Arthur D. Little, Inc., have also studied the removal of the pesticides alachlor, atrazine, carbaryl, pentachlorophenol, trifluralin, and diazinon from activated carbon (deFilippi and Murphy 1981). Although no specific studies on desorption of VOCs from activated carbon were encountered in the literature survey, the supercritical fluid process for regeneration of spent carbon needs to be evaluated further to see if it offers any economic and operational benefits.

#### 2.1.2.2 Catalytic Destruction

Another type of technology which has been used in industry to control the emission of VOCs from gas stream is catalytic destruction. In this process, a catalyst is used to promote the oxidation of organic compounds at lower temperature than required for thermal destruction. The catalyst increases the rate of the reaction by bringing the reactants together or by lowering the activation energy of the reaction. Approximately 500 to 2000 catalytic incinerators are currently used to control the emission of VOCs in various industries (Jennings et al. 1984).

The performance of a catalytic destruction device depends upon temperature, type and concentration of compounds, space velocity (residence time), and type of catalyst. A typical catalytic destruction system is usually composed of four basic parts. A preheater is used to bring the temperature of the incoming gas stream to approximately 600°F (315°C). A mixing chamber after the preheater is used to promote uniform temperature of the gas. Next, comes the catalyst bed itself. The catalyst is usually composed of either metal oxides or finely divided precious metal on either a metal or ceramic support structure. The catalytic system may be a fixed bed or fluidized system. The final part of the system is a heat recovery system which may be optional.

Spivey et al. (1987) conducted a literature review on heterogeneous catalytic destruction of potential environmentally hazardous compounds.

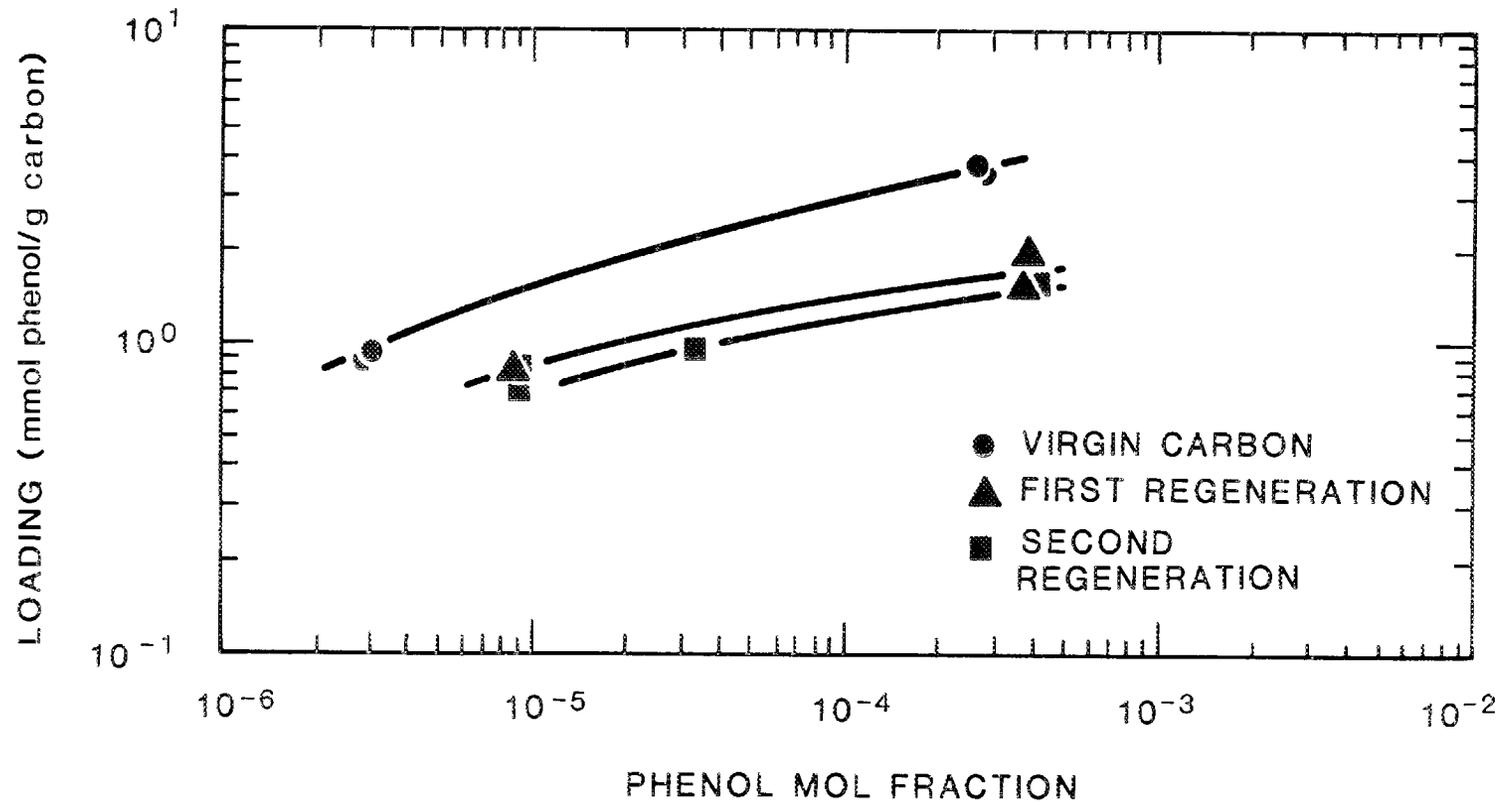


Fig. 6. Experimental adsorption isotherms for regenerated activated carbon (three cycles).

They present an excellent review on the mechanism of catalytic oxidation reactions and a comparison of metal oxide and precious metal catalysts. Listed below are some findings reported in their survey report:

1. Oxides of copper, manganese, cobalt, chromium and nickel are the most active, single-metal oxide, catalysts.
2. Mixed-metal oxide catalysts generally have higher activity than single metal oxide ones.
3. Metal oxide catalysts are less active than precious-metal catalysts; but the metal oxide catalysts are more resistant to certain poisons, such as halogens, arsenic, lead, and phosphorus.

Palazzolo et al. (1986) studied the destruction of mixtures of the halogenated hydrocarbons shown in Table 4 using fluidized-bed metal oxide catalyst and reports that the overall destruction efficiency varied from 97 to 99% for all the mixtures tested. He also noted that the catalyst inlet temperature had the largest effect on the destruction efficiency, while other variables such as mixture composition, air-to-fuel ratio, space velocity and inlet concentration only had a marginal effect on the destruction efficiency. The destruction efficiency of tetrachloroethylene was the lowest of all the compounds tested. The destruction efficiency across the preheater ranged from 15 to 55%.

An EPA survey on air strippers found only one use of a catalytic destruction device for emission controls (EPA-450/3-87-017). Even for this one test there was no performance data available. Thus, it is difficult to determine the cost and the problems which may be encountered with the use of a catalytic destruction device with air strippers.

#### 2.1.2.3 Thermal Incineration

Thermal incineration avoids the use of a catalyst and relies on heat energy to overcome the activation energy barrier of the oxidation reactions. Thermal incineration gives very high destruction efficiency and can be used when substances which poison a catalyst are present. The drawback of thermal incineration is the large amount of fuel needed to achieve the necessary temperatures [(1000 to 2500°F) (540 to 1370°C)]. Also, thermal incineration is usually better suited for streams which contain high concentration of VOCs.

Table 4. Mixture compositions and target concentrations  
for catalytic oxidation tests

Mixture designation	Concentration level	Mixture compounds	Target inlet concentration (ppmv) <sup>a</sup>
Mixture 1	Baseline	Trichloroethylene	6.3
		1,2 dichloroethylene	<u>8.5</u>
			14.8
Mixture 1	Low	Trichloroethylene	1.9
		1,2 dichloroethylene	<u>1.0</u>
			2.9
Mixture 2	Baseline	Trichloroethylene	2.7
		Benzene	1.5
		Ethylbenzene	5.6
		Pentane	11.5
		Cyclohexane	<u>14.1</u>
			35.4
Mixture 3	Baseline	Vinyl Chloride	7.5
		Trichloroethylene	<u>1.8</u>
			9.3
Mixture 4	Baseline	1,2 dichloroethane	10
		Trichloroethylene	10
		1,1,2-trichloroethane	10
		Tetrachloroethylene	<u>10</u>
			40
Mixture 4	High	1,2 dichloroethane	50
		Trichloroethylene	50
		1,1,2-trichloroethane	50
		Tetrachloroethylene	<u>50</u>
			200

<sup>a</sup>ppmv = parts per million by volume of the compound.

Source: Palazzolo, M. A., C. L. Jamgochain, J. I. Steinmetz, and D. L. Lewis, "Destruction of Chlorinated Hydrocarbons by Catalytic Oxidation," EPA-600/2-86-079, September 1986.

Jennings et al. (1984) compared vapor phase carbon adsorption, catalytic destruction, and thermal incineration with respect to general applicability, environmental and energy considerations, and operation and maintenance requirements. The results of their comparison are shown in Tables 5, 6, and 7.

#### 2.1.2.4 UV-Ozone Destruction

Ultraviolet light can be used in conjunction with ozone to oxidize organic compounds. A study by Palazzolo et al. (1986) indicated that the space velocity was the most important variable in destruction efficiency when ultraviolet light was used alone to promote the oxidation. The efficiencies during these tests ranged from 16 to 67%. When ultraviolet light was used in conjunction with ozone, almost complete oxidation (>99%) of the compounds in the mixture was achieved, but rather high concentrations of side reaction products were also detected.

#### 2.1.2.5 Membrane Separation

A considerable amount of research has been done in recent years on the use of membranes to separate various components from gas streams. Some of the work has been toward the purification of the solvent laden air stream coming from high temperature industrial ovens (Baker et al. and Peinemann et al.). Since most organic polymers are not useful at temperatures above 100°C, the use of silicone polymers has been investigated (Haggin 1987).

The air stream from stripping of volatile organics from groundwater operation is likely to be at ambient temperature and thus should not require the use of specially formulated membranes. The important variables in selecting a membrane are (1) the selectivity of the membrane for particular compounds and (2) the permeation rate of the compounds through the membrane. Since these two variables often have opposite effects on the overall process performance, optimization studies are usually required. Baker et al. found that selectivities greater than 100 to 200 are required if adequate separation from the air stream is to be obtained. They also report that separation of acetone and trichloroethane from air can be obtained using Fluorel® and neoprene, and that a number of materials provided adequate separation of toluene and octane.

Table 5. General applicability of control devices

Control device	Waste gas temperature requirements	Susceptibility to contaminants	Sensitivity to VOC species	Sensitivity to varying VOC concentrations	Size and space requirements	Emission stream and process data requirements
Carbon Adsorption	Stream must usually be less than 100°F. Cooler may be required.	Carbon is susceptible to fouling by high boiling point compounds such as resins.	Streams containing multiple VOCs will be more difficult to recover. VOCs miscible with water could require complex recovery treatment (i.e., distillation).	Recovery efficiency may vary.	Size is dependent on complexity of recovery system. Typical system requires as much or more land as thermal incinerator.	Requires more extensive data than other devices.
Catalytic Incinerator	Essentially none. Very high temperature streams (greater than 900°F) are unsuitable.	Catalyst is susceptible to erosion, masking and poisoning from particulate and catalyst poisons.	Operating temperature may be adjusted to achieve desired performance.	Little or none.	Smaller than thermal units. Can be used typically for roof installation.	Requires general process information, VOC waste gas stream characteristics (including presence of poisons and/or maskers).
Thermal Incineration (Recuperative)	None.	Corrosion can be a problem with certain contaminants.	Operating temperature may be adjusted to achieve desired performance.	Little or none.	Typically equivalent or higher than catalytic.	Minimal.
Thermal Incineration (Regenerative)	None.	Corrosion can be a problem with certain containments.	Operating temperature may be adjusted to performance.	Variability could affect energy use.	Typically not used for roof installation. Greater than conventional thermal system.	Minimal.

Sources: Jennings, M. S., N. E. Krohn, and R. S. Berry, "Control of Industrial VOC Emissions by Catalytic Incineration: Volume 1. Assessment of Catalytic Incineration and Competing Controls," EPA-600/2-84-118a, July 1984.

Table 6. Environmental and energy considerations

Control device	Potential overall VOC removal (%)	VOC removal variability	Secondary air pollution generation	Water pollution generation	Solid waste pollution generation	Supplemental energy use
Carbon Adsorption	95+	Potential for VOC removal efficiency to decrease with time. Efficiency depends on concentration.	Small amounts of particulate matter, SO <sub>2</sub> , and NO <sub>x</sub> from boiler used to generate steam.	VOC recovery process (i.e., decantation, distillation, extraction) create waste water containing VOC's.	Spent carbon must be either reactivated or disposed.	Depends on energy credit for recovered VOC's. Potentially very low or net credit.
Catalytic Incineration	95+	Potential for VOC removal efficiency to decrease with time.	Impurities such as nitrogen and sulfur in waste stream may cause emissions.	None.	Old catalyst support must be either reused or disposed.	Typically less than thermal incineration with recuperative heat exchange.
Thermal incineration (Recuperative)	95+ (Potentially greater than both catalytic incineration and adsorption).	Performance generally does not degrade with time.	Impurities such as nitrogen and sulfur in waste stream may cause emissions.	None.	None.	Potential highest depending on amount of heat recovery equipment used in the system.
Thermal Incineration (Regenerative)	95+ (Potentially greater than both catalytic incineration and adsorption.)	Performance generally does not degrade with time.	Impurities such as nitrogen and sulfur in waste stream may cause emissions.	None.	None.	Typically less than thermal incineration with recuperative heat exchange.

Source: Jennings, M. S., N. E. Krohn, and R. S. Berry, "Control of Industrial VOC Emissions by Catalytic Incineration: Volume 1. Assessment of Catalytic Incineration and Competing Controls," EPA-600/2-84-118a, July 1984.

Table 7. Operation and maintenance requirements

Control device	Overall equipment life	Overall reliability	Operation labor requirements	Maintenance labor and materials requirements	Startup/shutdown procedures	Potential for equipment damage
Carbon Adsorption	Approximately 10 years (except for carbon beds).	Potentially lower than incineration systems due to complexity.	Potentially high especially if distillation systems used. Skilled personnel may be required.	Potentially high with replacement of carbon beds at infrequent intervals.	Fairly complex depending on installation, however, very quick startup.	Somewhat greater than incineration, especially if stream is hot and cooling used.
Catalytic Incineration	Approximately 10 years (except for catalyst beds).	Approximately equivalent to thermal incineration systems except on dirty streams.	Low.	Low, unless emission stream dirty. Cleanings or replacement of catalyst at infrequent intervals.	Simple; need to bring temperatures up at controlled rate.	Somewhat greater potential than thermal.
Thermal Incineration (Regenerative)	Approximately 10 years.	Potentially highest due to simplicity; breakdown of refractory and insulation may be a problem due to high temperatures.	Low.	Low unless corrosive species present.	Simple; need to bring temperatures up at controlled rate.	Low unless corrosive species present.
Thermal Incineration (Regenerative)	Approximately 10 years.	Potentially lowest of incineration systems due to complexity.	Somewhat higher than other incineration systems, especially with fluctuating VOC loadings.	Low, however, maintenance of valves, dampers, and flappers can be high.	Fairly simple, however, procedures may be more complex than recuperative systems.	Low.

Source: Jennings, M. S., N. E. Krohn, and R. S. Berry, "Control of Industrial VOC Emissions by Catalytic Incineration: Volume 1. Assessment of Catalytic Incineration and Competing Controls," EPA-600/2-84-118a, July 1984.

Since purification of gas streams using membranes is still being researched in the laboratory, it is difficult to determine if this technology could be applied to air stripping operations successfully.

## 2.2 OTHER TECHNOLOGIES

### 2.2.1 Liquid-Phase Activated Carbon Adsorption

Removal of organic compounds from water using activated carbon is a well developed process. Although activated carbon can be used to remove a wide range of organic compounds, unsaturated organic compounds such as ethylenes are removed more effectively than saturated compounds (Dyksen 1982). To design an activated carbon system, experimental data are usually required to determine the capacity of the carbon for a particular compound. The Calgon Carbon Corporation has developed an accelerated carbon test which can be used to evaluate the feasibility of using activated carbon in much less time than conventional tests (Stenzel and Gupta 1985).

The packed carbon bed can be operated either as a gravity system or as a pressure system. The activated carbon system can also be classified as a pulse bed or multiple bed system. In the pulse bed system, a portion of the spent carbon is removed and replaced with fresh carbon after breakthrough occurs. A multiple bed system contains several beds which are used sequentially.

Although many small-scale activated carbon systems have been built and operated, few large-scale systems are in actual operation. Two large-scale operations were noted in the literature. One was used at Rockaway Township, New Jersey, to remove trichloroethylene (50 to 220 ppb), diisopropyl ether (up to 160 ppb), and methyl-tertiary-butyl ether (up to 50 ppb) (Althoff et al. 1981). The design parameters for the system were (McKinnon and Dyksen 1984):

Water flow rate	227 m <sup>3</sup> /h
Number of contactors	2
Contactors diameter	3.05 m
Contactors height	6.1 m
Amount of carbon per contactor	9072 kg
Contact time in the bed	12 min

The construction cost of the system in 1980 was \$245,000 (1987 dollars) and the operating cost was estimated to be \$0.64 per thousand gallons (3.79 m<sup>3</sup>) of water. The estimated lifetime of the carbon was expected to be between 6 to 8 months, but actual breakthrough of the ethers occurred after 4 months.

A second, full-scale activated carbon unit was operated at Wurtsmith Air Force Base, Oscoda, Michigan to remove trichloroethylene. The design of the system was based on a trichloroethylene concentration in the feed of 2000 ppb and a maximum effluent concentration of 5 ppb. The system parameters were (Gross, 1985):

Water flow rate	272 m <sup>3</sup> /h
Number of beds	3
Carbon per bed	9072 kg

The estimated capital cost of the system was \$1,527,000 (1987 dollars) and annual operating cost was near \$394,000 (Gross and TerMaath 1985). The total cost of treatment per thousand gallons (3.79 m<sup>3</sup>) was \$0.96. The major operating cost was in the replacement of the carbon, which was estimated to be 81,647 kg/year.

Because the cost of replacing the carbon is so high, on site regeneration may be more economical in the long range. The regeneration technologies have been previously discussed in Sect. 2.1.2.1, which is the section on emission control from air strippers. IT Corporation has performed cost analyses of liquid-phase carbon adsorption with on-site steam regeneration of the loaded carbon (Parmele et al. 1986). Their cost analysis indicated that when the water flow is greater than 100 gpm (22.7 m<sup>3</sup>/h) and treatment is required for several years, liquid phase carbon adsorption with on-site steam-regeneration is a cost-effective alternative to air stripping when greater than 99% removal of VOCs is required.

#### 2.2.2. Membrane Separation

Separation of VOCs from water using membranes may be one of the most promising technologies for the future. Membrane separation will not be a

stand-alone process, but it could be used in conjunction with other treatment processes to make the overall process more cost effective. A hybrid membrane separation and air stripping without emission control process could be economically competitive (Weber and Bowman, 1986). In this process, a membrane system is first used to reduce the volatile organic concentration in the water by 85 to 90%. The clean water stream from the membrane system is then put through an air stripper which further reduces the VOCs in the water. Using the air stripper after the membrane system avoids the need for expensive emission control devices because the contaminant concentrations are greatly reduced in the influent water to the air stripper. Again, due to lack of pilot-scale data, it is difficult to evaluate this technology in great detail.

### 2.2.3 Biological Treatment

In situ biological treatment of aquifers contaminated with VOCs has received some attention in recent years because hydrocarbon-degrading microorganisms have been discovered in groundwater (Wilson and McNabb 1983 and Wilson et al. 1983). Fuel oil components are easily degraded by microorganisms under aerobic conditions. The degradation of chlorinated solvents has been noted under both aerobic and anaerobic conditions although the exact mechanisms are not well understood.

The low amount of dissolved oxygen in groundwater is often the limiting factor in the in situ destruction of organic compounds. Several studies have been conducted in which oxygen and nutrients have been added to the contaminated groundwater to stimulate biodegradation of VOCs (Yaniga and Smith 1985, Ohneck and Gardner 1982, Yaniga 1982, Wetzel et al. 1987, Downey et al. 1987).

Ohneck and Gardner inoculated the effluent from the liquid-phase adsorption treatment process with hydrocarbon-degrading bacteria and nutrients prior to reinjection. The dissolved oxygen content of the water was also increased prior to reinjection. The main purpose of this treatment was to establish biological growth around the soil particles in the vadose (unsaturated soil) zone to degrade chemicals entrapped in the soil. Ohneck and Gardner report that "with the addition of the biological treatment, cleanup effectiveness was increased while the costs of the operation and maintenance were decreased."

Yaniga and Smith used air stripping and in situ biological treatment to remove benzene, toluene, and xylene from groundwater. They report the use of hydrogen peroxide as a source of oxygen to enhance biological growth. The hydrogen peroxide was added to the effluent from the air stripper prior to reinjection and was also introduced into the groundwater through a well. An advantage of using hydrogen peroxide is that dissolved oxygen concentration is not limited by the mass transfer equipment. The disadvantages of using hydrogen peroxide include (1) the high cost of hydrogen peroxide, (2) toxicity to microbes at levels above 50 to 100 mg/L, and (3) precipitation of minerals caused by reaction with hydrogen peroxide which results in decreased permeability of the soil.

One of the limitations of in situ biological treatment has been the ability to transfer the technology from the laboratory to the field. Problems associated with the delivery of chemicals required to enhance biological growth in the subsurface environment have not been resolved. Also, in situ biological treatment by itself will not be a cost-effective technology in the treatment of groundwater which contains relatively large amounts of contaminants.

Aboveground biological treatment may also be used to remove VOCs from groundwater. The treatment can be accomplished using either a suspended growth reactor or an attached growth reactor, such as a rotating biological contactor. The design procedure and performance of these reactors can be found in many wastewater treatment textbooks (Metcalf & Eddy, Inc., 1979; Benefield and Randall 1980).

#### 2.2.4 Chemical Oxidation

Chemical oxidation is used in water and wastewater treatment to convert undesirable chemicals into compounds which are less objectionable. The oxidizing agents which have been used in water and wastewater treatment include: (1) oxygen or air, (2) ozone, (3) hydrogen peroxide, (4) potassium permanganate, (5) chlorine or hypochlorites, and (6) chlorine dioxide (Weber 1972).

In recent years, ultraviolet light has been used in combination with oxidizing agents to make the chemical oxidation process more effective. The United States Army has investigated ozone oxidation with ultraviolet light to treat the wastewater from mobile field hospitals called MUST

[Medical Unit, Self-contained, Transportable] (McCarthy 1977). This study was conducted with synthetic laboratory waste which contained the following compounds: diethyl ether, methanol, urea, glycerol, ethanol, 10% formaldehyde, o-phenylphenol, o-benzyl-p-chlorophenol, xlenol, isopropanol, and acetone. The rate of chemical destruction was unexpectedly low in all the experiments. It was postulated that the low destruction was caused by an insufficient concentration of ozone in the water (0.1 to 0.4 mg/L). The destruction of methanol was most affected by the dissolved concentration of the ozone and the destruction of acetone was affected by the absence or presence of ultraviolet light.

The United States Navy has investigated the use of ultraviolet light and hydrogen peroxide to treat trinitrotoluene contaminated wastewater (Andrews 1980). The treatment process was found to be effective in treating the contaminated wastewater and was found to be more economical than ultraviolet light-ozone treatment or carbon adsorption.

### 3. SUMMARY

Several technologies are available for the removal of VOCs from groundwater including (1) air stripping, (2) biological treatment, (3) carbon adsorption, (4) chemical oxidation, and (5) membrane separation. Of these technologies, only air stripping and carbon adsorption have been used in large-scale operations. The design procedure for a packed air stripper is well developed with several correlations available to estimate mass transfer coefficients. Carbon adsorption usually requires laboratory studies to size full-scale units. One of the problems with using air stripping is the emission of VOCs in the air stream. The cleanup of the air stream can be accomplished using vapor-phase carbon adsorption, catalytic destruction, or thermal destruction.

Although some numbers are available in the literature on the cost of each technology, the data base is insufficient to reach any definite conclusions.

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APPENDICES

APPENDIX A  
MASS-TRANSFER MODELS

The transfer unit concept for generalization of anticipated air stripping tests seems very appropriate due to its inherent simplicity and acceptance by design engineers. This concept is well established for generalization of packed tower performance. The possibility of its applicability to centrifugal contactor operation seems reasonable, based on it being a type of packed gas-liquid contactor. A schematic drawing of a typical packed gas-liquid contactor is shown in Fig. A.1. A material balance around the lower section of the contactor yields

$$Lx + G_1y_1 = L_1x_1 + Gy \quad (\text{A.1})$$

Differentiating this equation yields

$$d(Lx) = d(Gy), \quad (\text{A.2})$$

which represents the rate of mass transfer and may be expressed as

$$d(Lx) = N_A adZ. \quad (\text{A.3})$$

The mol fractions of the transferring species are expected to be dilute so that little loss of accuracy results from the assumption that the liquid and gas molar velocities are constant in contactors with constant cross-sectional area. For contactors of varying cross-sectional area, an average  $L$  may be used, at least for initial calculations; otherwise  $L$  will be a function of  $Z$ . For dilute solutions, it is also likely that the equilibrium distribution ratio is also constant and the mass-transfer flux may be described in terms of an overall coefficient and driving force

$$N_A = K_X (x - y/m) \quad (\text{A.4})$$

where the overall coefficient is related to the individual phase coefficients by

ORNL DWG 88-66

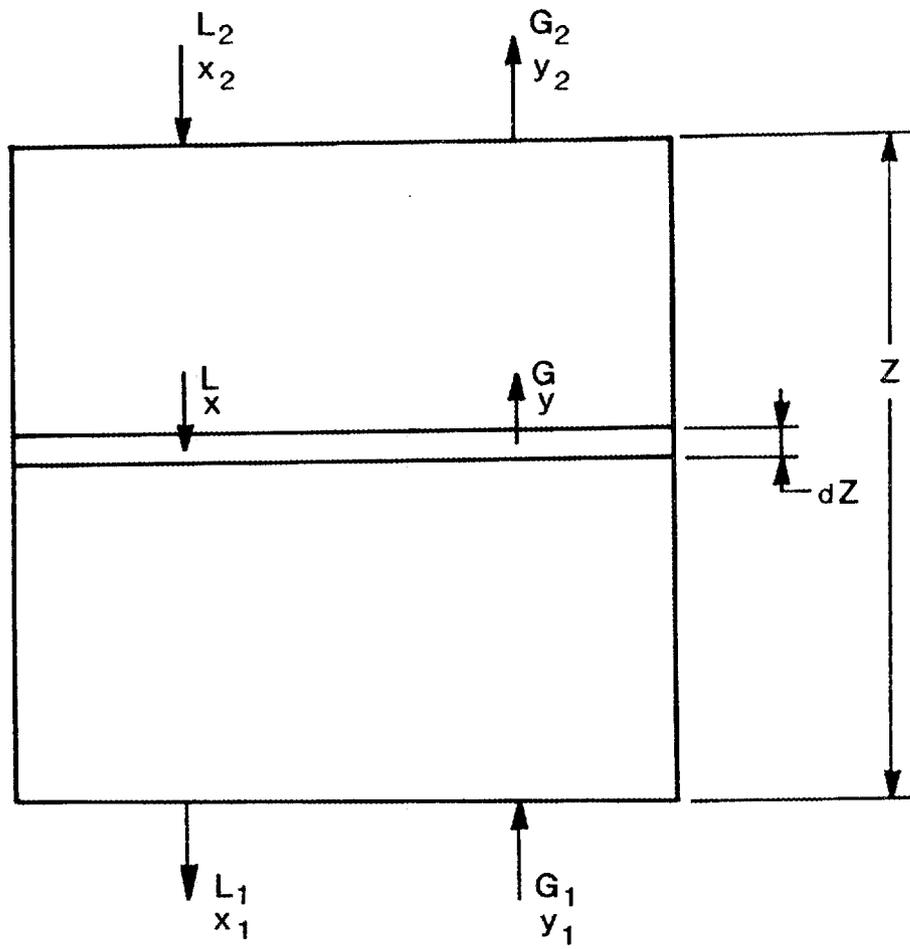


Fig. A.1. Packed gas-liquid absorber.

$$\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{mk_y}. \quad (\text{A.5})$$

The differential material balance may be related to the mass-transfer flux equation by

$$Ldx = Gdy = N_A adZ. \quad (\text{A.6})$$

Focusing on the liquid phase elements of this expression yields

$$Ldx = K_x a (x - y/m) dZ. \quad (\text{A.7})$$

Separation of variables and imposition of limits of integration yields the following

$$\int_0^Z dZ = \frac{L}{K_x a} \int_{x_1}^{x_2} \frac{dx}{x - y/m} \quad (\text{A.8})$$

The expression is now in the form of

$$Z = H_{toL} N_{toL}. \quad (2)$$

where  $N_{toL}$  and  $H_{toL}$  are the height and number of overall liquid-phase transfer units and may be expressed as

$$H_{toL} = L/K_x a \quad (4)$$

and

$$N_{toL} = \int_{x_1}^{x_2} \frac{dx}{x - y/m} \quad (7)$$

This equation is easily integrated (Sherwood et al. 1975) by defining

$$\Delta = x - y/m. \quad (\text{A.9})$$

Since the quantities  $m$  and  $L/G$  have been assumed to be reasonably constant,

$$\frac{d\Delta}{dx} = \frac{\Delta_2 - \Delta_1}{x_2 - x_1} \quad (\text{A.10})$$

and

$$N_{\text{toL}} = \frac{x_2 - x_1}{\Delta_2 - \Delta_1} \int_{\Delta_1}^{\Delta_2} \frac{d\Delta}{\Delta} \quad (\text{A.11})$$

Integration yields

$$N_{\text{toL}} = \frac{x_2 - x_1}{\Delta_2 - \Delta_1} \ln \frac{\Delta_2}{\Delta_1} = \frac{x_2 - x_1}{\Delta_M} \quad (\text{A.12})$$

or

$$N_{\text{toL}} = \frac{x_2 - x_1}{(x - y/m)_M} \quad (\text{A.13})$$

Gas-phase compositional analysis is not required;  $y$  may be found from the original material balance expression, which now incorporates the assumption of a constant ratio of liquid to gas molar velocities,

$$y = y_1 + (L/G) (x - x_1). \quad (\text{A.14})$$

The expression for the number of overall liquid-phase transfer units now becomes

$$N_{\text{toL}} = \int_{x_1}^{x_2} \frac{dx}{x - y_1/m - (L/mG) (x - x_1)}. \quad (\text{A.15})$$

If the quantity  $mG/L$  is defined as

$$S = mG/L, \quad (1)$$

then

$$N_{toL} = \int_{x_1}^{x_2} \frac{dx}{x - y_1/m - (x - x_1)/S} \quad (A.16)$$

The quantity  $S$  is commonly known as a stripping factor. The integrated version of this equation (Colburn 1941) is

$$N_{toL} = \frac{\ln \left[ \left( \frac{x_2 - y_1/m}{x_1 - y_1/m} \right) (1 - 1/S) + (1/S) \right]}{(1 - 1/S)} \quad (A.17)$$

For stripping,  $y_1$  is expected to be zero so that these equations may be simplified to

$$N_{toL} = \int_{x_1}^{x_2} \frac{dx}{x - (x - x_1)/S} \quad (A.18)$$

and

$$N_{toL} = \frac{\ln \left[ \left( \frac{x_2}{x_1} \right) (1 - 1/S) + (1/S) \right]}{(1 - 1/S)} \quad (A.19)$$

## APPENDIX B

MASS TRANSFER CORRELATIONS FOR CONVENTIONAL-PACKED  
GAS-LIQUID CONTACTORS

The height of an overall liquid-phase transfer unit for dilute solutions of the transferring component ( $y$  &  $x \approx 0$ ) may be represented by

$$H_{toL} = H_L + H_G/S. \quad (3)$$

An extensive discussion of modeling mass-transfer in packed towers is presented by Fair et al. (1984). A generalized equation for the height of a liquid phase transfer unit developed by Cornell et al. (1960) and refined by Bolles and Fair (1982) is

$$H_L = \frac{\phi C}{3.28} \left( \frac{\mu_L}{\rho_L D_L} \right)^{0.5} \left( \frac{Z_p}{3.05} \right)^{0.15} \quad (B.1)$$

The coefficient  $C$  is designed to account for the reduction in  $H_{toL}$  as the flooding point is approached; it is a function of the ratio of the gas mass velocity to that at flooding at constant  $L'/G'$ . This coefficient may be estimated by a procedure by Coulson et al. (1983) or from Fig. 18.59 of Fair et al. (1984). The correlation parameter  $\phi$  was adjusted by Bolles and Fair (1982) to give an improved fit of a large body of data for ceramic Raschig rings and Berl saddles as well as metal Raschig rings and Pall rings and may be estimated from Fig. 18.60 of Fair et al. (1984). This equation retains Cornell's original correction factor ( $Z_p/3.05$ ); the "standard" value of  $Z_p$  used in these tests was 3.05m. This correction factor should only be used when the distance between liquid redistributors is over 3.05 m.

An estimate of  $H_L$  may also be obtained using the liquid-phase mass-transfer coefficient

$$H_L = \frac{L'}{k_L a \rho_L} \quad (B.2)$$

or

$$H_L = \frac{L}{k_x a} \quad (\text{B.3})$$

The mass-transfer coefficient  $k_L$  is related to  $k_x$  by

$$k_x = k_L \rho_L / M_L \quad (\text{B.4})$$

In terms of film theory, these individual phase coefficients  $k_x$ ,  $k_L$ ,  $k_G$ ,  $k_y$ , etc., are those for the transfer of a component through an otherwise stagnant film.

The coefficient "a" is often approximated by the use of  $a_w$  (the wetted area of packing per unit volume).

Onda et al. (1968) correlated a large amount of liquid-phase transfer data to  $\pm 20$  percent by the equation

$$k_L \left( \frac{\rho_L}{\mu_{LE}} \right)^{1/3} = 0.0051 \left( \frac{L'}{a_w \mu_L} \right)^{2/3} \left( \frac{\mu_L}{\rho_L D_L} \right)^{0.50} (a_t d_p)^{0.4} \quad (\text{B.5})$$

which is dimensionally consistent. In this equation  $a_w$  is the wetted surface of the packing obtained from

$$\frac{a_w}{a_t} = 1 - \exp \left[ - \left[ 1.45 \left( \frac{\sigma_c}{\sigma} \right)^{0.75} \text{Re}_L^{0.1} \text{Fr}_L^{-0.05} \text{We}_L^{0.2} \right] \right] \quad (\text{B.6})$$

with the Reynolds, Froude, and Weber groups being dimensionless. This equation is based on experimental data for organic liquids, as well as for water. Packings included are Raschig rings, 6 to 50 mm (1/4 to 2 in.); Berl saddles, 12 to 38 mm (1/2 to 1 1/2 in.); 25-mm (1-in.) Pall rings; 12- and 25-mm (1/2- and 1-in.) spheres; and 12- and 25-mm (1/2- and 1-in.) rods. The critical surface tension of several packing materials is presented in Table B.1. The range of conditions covered by the experiments is given by

Table B.1. Critical surface tension of packing materials

	$\sigma_c$ [mN/m(dyn/cm)]
Carbon	56
Ceramic	61
Glass	73
Paraffin	20
Polyethylene	33
Polyvinylchloride	40
Steel	75

Source: Fair, Steinmeyer, Penny, and Crocker, "Liquid-Gas Systems" of Perry's Chemical Engineering Handbook Sixth Ed. (Perry, Green and Maloney, Editors), 18-34 (1984).

Table B.2. Range of variables and physical properties for the Mohunta Correlation (Mohunta et al. 1969a)

Variables	Range
$L'$	0.1 to 42 kg/m <sup>2</sup> -s
$G'$	0.015 to 1.22 kg/m <sup>2</sup> -s
$\mu_L$	0.7 to 1.5 mN/m <sup>2</sup> -s
$\mu_L/\rho_L D_L$	142 to 1033
$d_c$	6 to 50 cm
$d_p$	0.6 to 5.1 cm
$d_c/d_p$	5 to 40

Source: Mohunta, D. M., A. S. Vaidyanathan, and G. S. Laddha, "Predictions of Liquid-Phase Mass Transfer Coefficients in Columns Packed with Raschig Rings," Indian Chem. Eng., 11(3), 73-79, 1969.

$$\begin{aligned}
0.04 < \text{Re}_L < 500 \\
1.2 \times 10^{-8} < \text{We}_L < 0.27 \\
2.5 \times 10^{-9} < \text{Fr}_L < 1.8 \times 10^{-2} \\
0.3 < \frac{\sigma_c}{\sigma} < 2.
\end{aligned}$$

Mohunta et al. (1969a) developed a generalized correlation based on their experiments with ceramic 10-, 13-, and 19-mm Raschig rings and other published data for ceramic Raschig rings in sizes from 6 to 51 mm that summarized approximately 80% of the literature results to about  $\pm 20$  percent; the maximum deviation was within  $\pm 40\%$ . Their equation is

$$k_L a \left( \frac{a_t \mu_L}{\rho_L g} \right)^{2/3} \left( \frac{\mu_L}{\rho_L g^2} \right)^{1/9} = 0.0025 \left( \frac{\mu_L (L')^3 a_t^2}{\rho_L^4 g^2} \right)^{1/4} \left( \frac{\mu_L}{\rho_L D_L} \right)^{-1/2} \quad (\text{B.7})$$

Their form of the interfacial area equation (Mohunta 1969b) is

$$\frac{a}{a_t} = 0.175 \left( \frac{L'}{a_t \mu} \right)^{1/3} \quad (\text{B.8})$$

This equation is based on experiments with towers packed with 10-, 13-, and 19-mm Raschig rings. The range of variables and physical properties for this correlation is presented in Table B.2.

Generalized equations for the height of a gas-phase transfer unit developed by Cornell et al. (1960) and later refined by Bolles and Fair (1982) are

$$H_G = \frac{0.017 \psi d_c^{1.24} Z_p^{0.33} S_{cG}^{0.5}}{(L' f_1 f_2 f_3)^{0.6}} \quad (\text{B.9})$$

for ring-type packing, and

$$H_G = \frac{0.029 \psi d_c^{1.11} Z_p^{0.33} S_{cG}^{0.5}}{(L' f_1 f_2 f_3)^{0.5}} \quad (\text{B.10})$$

for saddle-like packing.

The correlation parameter  $\psi$  was adjusted by Bolles and Fair (1982) to give an improved fit of a large body of data covering additional packing types. Values of the adjusted parameters may be obtained from Fig. 18-65 of Fair et al. (1984). In the use of this equation, there is the

following restriction: for column diameters larger than 0.6 m (2.0 ft), retain the previous diameter correction for 0.6 m (Fair et al. 1984).

An estimate of  $H_G$  may be obtained using the gas-phase mass transfer coefficient

$$H_G = \frac{G}{k_y a} \quad (\text{B.11})$$

or

$$H_G = \frac{G'}{k_g a P_T M_G} \quad (\text{B.12})$$

The coefficient  $k_g$  is related to  $k_y$  by

$$k_y = k_g P_T \quad (\text{B.13})$$

Onda et al. (1968) correlated available gas-phase absorption data with the dimensionless equation

$$\frac{k_G RT}{a_t D_G} = C_1 \left( \frac{G'}{a_t \mu_G} \right)^{0.7} \left( \frac{\mu_G}{\rho_G D_G} \right)^{1/3} (a_t d_p)^{-2.0} \quad (\text{B.14})$$

where the constant  $C_1$  is 5.23 for ring and saddle packings larger than about 12 mm (1/2 in.). For smaller packings the value of  $C_1$  is 2.00. It should be noted that the area term used is that of the total external surface of the packing material. For desorption data, the use of the above equation and a  $C_1$  of 5.23 described most of the data fairly well. However, these tests primarily involved packings of sizes greater than 13 mm. Packings represented by the data are essentially those used previously to determine liquid-phase coefficients.

Another equation for the gas-phase mass-transfer coefficient presented by Joshi et al. (1985) is

$$\frac{(k_G RT) \ell}{D_G} = 0.553 \frac{(P_m \ell)^{1/3} \ell \rho_G}{\mu_G} (Sc_G)^{1/3} \frac{P_T}{P_I} \quad (\text{B.15})$$

where,  $P_m$  is the power consumption per unit mass of the gas,

$$P_m = \frac{f a_t}{6(\epsilon - \epsilon_L)^4} V_G^3 \quad (\text{B.16})$$

The value of  $l$  depends upon the type of the packing,

$$l = 0.5d_p \text{ for Raschig rings,} \quad (\text{B.17})$$

$$l = 0.25d_p \text{ for Intalox saddles, and} \quad (\text{B.18})$$

$$l = 0.1d_p \text{ for Pall rings.} \quad (\text{B.19})$$

Joshi et al. (1985) also presented correlations for the effective interfacial area; these are summarized in Table B.3.

Another source of information on  $k_L$  and "a" for packing sizes up to 38 mm is found in Danckwerts (1970).

The mass-transfer characteristics of slotted plastic packing were investigated by Kshirsagan and Pangarkar (1984). The packings used in the study all had characteristic diameters of 25 mm. They were Pall rings, modified Pall rings (Hypack<sup>R</sup>), and a tapered Pall ring (with a length to diameter ratio  $<1$ ). The following equations give the hold-up correlations for air-water systems with conventional, modified and tapered Pall rings, respectively:

$$\epsilon_L = 0.029 V_L^{0.47} , \quad (\text{B.20})$$

$$\epsilon_L = 0.037 V_L^{0.50} , \text{ and} \quad (\text{B.21})$$

$$\epsilon_L = 0.030 V_L^{0.48} . \quad (\text{B.22})$$

The modified Pall ring gives much higher (50%) values of  $k_L a$  than for the conventional Pall rings. The  $k_L a$  measurements were determined using the absorption of  $\text{CO}_2$  into aqueous solutions of sodium carbonate - sodium bicarbonate. The tapered Pall ring gave the poorest values of  $k_L a$  of the three packings tested. The data were correlated by the following equations for conventional, modified, and tapered Pall rings, respectively:

Table B.3. Correlations for effective interfacial area  
in packed columns

Packing type	Material	Size (mm)	$V_L$ (mm/s)	a
Raschig rings	Ceramic	$6 < d_p < 89$	$0 < 15$	$8.0 V_L^{0.403} d_p^{-1.015} / \epsilon^3$
Intalox saddles	Ceramic	$6 < d_p < 76$	$0 < 12$	$19.6 V_L^{0.478} d_p^{-1.0} / \epsilon^3$
Intalox saddles	Polypropylene	$d_p = 25.4$	$0 < 10$	$14.2 V_L^{0.478} d_p^{-1.0} / \epsilon^3$
Pall rings	Stainless steel	$12 < d_p < 89$	$0 < 10$	$28.4 V_L^{0.5} d_p^{-1.07} / \epsilon^3$
Pall rings	Polypropylene	$d_p = 25.4$	$0 < 10$	$16.3 V_L^{0.5} d_p^{-1.07} / \epsilon^3$

Source: Joshi, Mahajani, and Juvekar, Chem. Eng. Sci. 33, 1 (1985).

$$k_{La} = 0.0027 V_L^{1.15}, \quad (\text{B.23})$$

$$k_{La} = 0.007 V_L^{0.91}, \text{ and} \quad (\text{B.24})$$

$$k_{La} = 0.0046 V_L^{0.80}. \quad (\text{B.25})$$

The mass-transfer characteristics of 38-mm stainless steel Pall rings, 38-mm polypropylene Pall rings, 38-mm polypropylene Intalox saddles, 50-mm carbon steel Pall rings, and 50-mm polypropylene Pall rings were investigated by Dharwadkar and Sawant (1984). The liquid holdup data for the air-water system were correlated by the equation

$$\epsilon_L = aV_L^b. \quad (\text{B.26})$$

The constants  $a$  and  $b$  are given in Table B.4. The highest values of  $k_{La}$  at a given  $V_L$  were obtained using the 38-mm stainless steel Pall rings; the values of  $k_{La}$  for polypropylene Pall rings are 15 to 50% lower than metal Pall rings of corresponding sizes at a given  $V_L$ . The  $k_{La}$  data were correlated by the equation

$$k_{La} = gV_L^h. \quad (\text{B.27})$$

The constants  $g$  and  $h$  obtained for various packings are tabulated in Table B.5.

A review of methods for predicting mass-transfer coefficients and interfacial areas for, primarily, bluff-body random packings was presented by Laurent and Charpenier (1974). They recommend use of the equation of Mohunta et al. (1969a) for  $k_{La}$  predictions. They indicate that the interfacial area prediction equation of Onda et al. (1968) should be accurate to  $\pm 20\%$  except for Pall rings where the interfacial area is underpredicted by about 50%. They recommend the following equation for  $k_G$  predictions with  $\pm 30\%$  accuracy:

$$\frac{k_G P}{G} = \frac{C_1}{M_G} (a_t d_p)^{-1.7} \left( \frac{G' d_p}{\mu_G} \right)^{-0.3} \left( \frac{\mu_G}{\rho_G D_G} \right)^{-0.5}, \quad (\text{B.28})$$

where  $C_1 = 2.3$  for packing with  $d_p < 15$  mm and 5.23 for  $d_p > 15$  mm.

Table B.4. Constants and exponents for liquid holdup prediction  
for work of Dharwadkar and Sawant

Packing	a	b
0.038 m stainless steel Pall ring	0.5969	0.4057
0.038 m polypropylene Pall ring	0.7530	0.4815
0.038 m polypropylene Intalox saddle	0.8304	0.6093
0.05 m carbon steel Pall ring	0.8746	0.5426
0.05 m polypropylene Pall ring	2.9824	0.8107

Source: Dharwadkar, S. W. and S. B. Sawant, "Mass Transfer and Hydrodynamic Characteristics of Tower Packing Larger Than 0.025 m Nominal Size," Chem. Eng. J., 31, 15-21, 1985.

Table B.5. Constants and exponents for  $k_L a$  prediction  
for work of Dharwadkar and Sawant

Packing	g	h
0.038 m stainless steel Pall ring	0.4839	0.6468
0.038 m polypropylene Pall ring	3.8719	1.0679
0.038 m polypropylene Intalox saddle	0.9281	0.9026
0.05 m carbon steel Pall ring	0.3360	0.6659
0.05 m polypropylene Pall ring	0.1688	0.5670

Source: Dharwadker, S. W. and S. B. Sawant, "Mass Transfer and Hydrodynamic Characteristics of Tower Packing Larger Than 0.025 m Nominal Size," Chem. Eng. J., 31, 15-21, 1985.

Krotzsch (1982) compared predictions for  $k_L a$  from several sources with experimental data from several commercial dumped plastic packings, including 25-mm Pall rings, 25-mm Tellerettes, and 25-mm Intalox saddles. They found that the equations of Mohunto et al. (1969a) agreed best with the experimental data, and that the results were within the error range of  $k_L a$  values predicted from the equation of Onda et al. (1968).

Mass transfer information on metal gauze packing (Sulzer BX) was presented by Bravo et al. (1985). The data base for the information in that work was from distillation experiments. Their models are

$$Sh'_G = 0.0338 Re'_G{}^{0.8} Sc_G{}^{0.333} , \quad (B.29)$$

$$k_L = 2 (D_L V'_L / \pi Z_{CS})^{0.5} , \text{ and} \quad (B.30)$$

$$a = a_t . \quad (B.31)$$

Several quantities in these equations require further explanation; including:

$$Sh'_G = k_G d_{eq} / D_G , \quad (B.32)$$

$$Re'_G = (d_{eq} \rho_G / \mu_G) (V'_G + V'_L) , \quad (B.33)$$

$$d_{eq} = 4r_h = 4 (\text{flow area/perimeter}) , \quad (B.34)$$

$$V'_L = (3\Gamma / 2\rho_L) (\rho_L^2 g / 3\mu_L \Gamma)^{0.333} , \text{ and} \quad (B.35)$$

$$V'_G = V_G / \epsilon \sin \theta . \quad (B.36)$$

The data base for these correlations consisted of experiments where the mass-transfer resistance was primarily in the gas-phase. This equation for  $k_L$  appears to underestimate experimental values of  $k_L$  observed by Kiranjan and Pangarkar (1983), and Selby and Counce (1988). Selby and Counce (1987) observed  $k_L$  values for the Koch Sulzer-type BX plastic packing of approximately an order of magnitude higher than those typical of standard bluff-body packings. The correlations of Bravo et al. (1985)

should be useful for estimating the mass transfer properties for metal or plastic gauze packing, provided however, that the packing surface is wet by the liquid phase.



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